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FIELD OF SOLID SOLUTIONS FORMED BY CELSIAN, DIBARIUM TRISILICATE, AND BARIUM DISILICATE (SANBORNITE)

N. A. Toropov, F. Ya. Galakhov and I. A. Bondar

The study of temary solid solutions in the three-component system $BaO-Al_2O_3-SiO_2$ presents great interest. In silicate systems, as also in metal systems, cases in which binary solid solutions areformed are very numerous. Earlier investigations of the binary system $BaO-SiO_2$ [1], which is included in the ternary system $BaO-Al_2O_3-SiO_2$ with which we are now concerned, indicated the existence of a continuous series of solid solutions formed between two intermediate compounds, dibarium trisilicate ($2BaO \cdot 3SiO_2$) and sanbornite ($BaO \cdot 2SiO_2$). No data existed, however, concerning the behavior of alumina when added to this binary solid solution.

Only comparatively recently Thomas [2] has noted that alumina dissolves in the binary solid solution $BaO \cdot 2SiO_2 - 2BaO \cdot 3SiO_2$, i.e., forms a ternary solid solution between celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$), sanbornite ($BaO \cdot 2SiO_2$), and dibarium trisilicate ($2BaO \cdot 3SiO_2$). Attention must be drawn, however, to a certain inconsistency between the binary vertical sections $2BaO \cdot 3SiO_2 - BaO \cdot Al_2O_3 \cdot 2SiO_2$ and $BaO \cdot 2SiO_2 - BaO \cdot Al_2O_3 \cdot 2SiO_2$ given by the author and the values of the refractive indices of the crystals separated in this field.

The sections indicate that celsian has limited solubility both in sanbornite and in dibarium trisilicate, whereas the variation in refractive index presents a picture of an unlimited series of solid solutions between these phases. The author takes the refractive index of celsian as equal to that of the limiting solid solution. For example, at a composition of 50% $BaO \cdot 2SiO_2$ and 50% $BaO \cdot Al_2O_3 \cdot 2SiO_2$, at which, according to the diagram, celsian should be observed as the primary phase, Thomas noted the presence only of a solid solution of refractive index $n_g = 1.600$ and $n_p = 1.588$. Actually, however, this refractive index is characteristic not of a solid solution, but of pure celsian.

EXPERIMENTAL

The object of our work was the detailed verification of the existence of a field of ternary solid solutions, the establishment of the boundaries of this field, and the study of its liquidus surface. We have studied a field that is contiguous with the line $2BaO \cdot 3SiO_2 - BaO \cdot 2SiO_2$, and also with part of the field of barium metasilicate ($BaO \cdot SiO_2$), sanbornite ($BaO \cdot 2SiO_2$), and celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$) (Fig. 1).

In the synthesis of the samples the following materials were used: 1) silica, as a fine powder prepared from rock crystal (99.9% SiO_2); 2) concentrated alumina (total impurity 0.2%); 3) barium carbonate ("chemically pure", containing 99.95% $BaCO_3$). Homogeneity was attained in the samples by melting them in an electric arc. The necessary amounts of the original materials were weighed out on an analytical balance and carefully mixed by being ground together in a mortar. The mixture was moistened with a solution of dextrin and formed into rods, 3-4 mm in diameter, with the aid of a glass tube. The samples were dried, and then fused in the electric arc.

The investigation was carried out by the quenching method, the samples being examined microscopically and subjected to X-ray analysis.

The optical study was carried out mainly by the immersion method; in certain cases combined slides were made for transmitted and reflected light. Preliminary observations showed that for all of the compositions studied the initial crystallization temperatures were about 1450°. A platinum furnace was, therefore, used, except for some samples containing a large amount of alumina (over 10%), for which a platinum-rhodium (20% Rh) furnace was used, since the temperature at which the primary phase separated was higher than 1450°.

TABLE

Composition (% by wt.)			Temperature of liquidus (°C)	Refractive indices of glasses	Primary phase	Refractive indices of crystals		
BaO	Al_2O_3	SiO_2				n_g	n_p	mean
52	3	45	1315	1.587	$BaO \cdot 2SiO_2$	1.621•	1.597•	1.609•
55	3	42	1350	1.600	Solid solution	1.619	1.597	1.608
58	3	39	1360	1.613	" "	1.628	1.605	1.616
61	3	36	1375	1.626	" "	1.634	1.609	1.622
64	3	33	1380	1.639	$BaO \cdot SiO_2$	1.678	1.673	1.675
49	6	45	1285		$BaO \cdot 2SiO_2$			
52	6	42	1320	1.595	Solid solution	1.616	1.593	1.604
55	6	39	1330	1.607	" "	1.627	1.604	1.614
58	6	36	1340	1.617	" "	1.632	1.608	1.619
61	6	33	1350		$BaO \cdot SiO_2$			
46	9	45	1240		$BaO \cdot 2SiO_2$			
49	9	42	1275	1.586	Solid solution	1.604	1.589	1.597
52	9	39	1300	1.598	" "	1.611	1.594	1.603
55	9	36	1310	1.610	" "	1.616	1.600	1.608
58	9	33	1320		$BaO \cdot SiO_2$			
43	12	45	1380		$BaO \cdot Al_2O_3 \cdot 2SiO_2$			
46	12	42	1405	1.578	The same	1.600•	1.588•	1.594•
49	12	39	1430		"			
52	12	36	1450		"			
55	12	33	1475		"			

• Eskola's data [1].

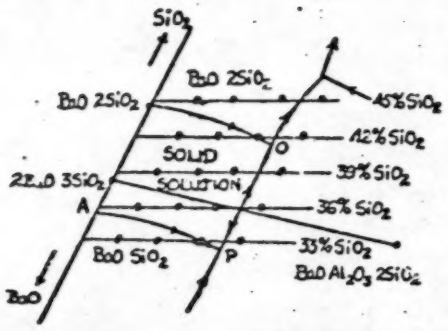

Fig. 1. Field of ternary solid solutions.

As investigation showed (Fig. 1), a field of solid solutions occurs in the ternary diagram, and they contain up to about 10% Al_2O_3. At a higher alumina content we reach the field of the primary crystallization of celsian. The positions of the boundary lines of the field of ternary solid solutions with barium metasilicate on the one side (A—P) and solid solution and barium disilicate ($BaO \cdot 2SiO_2$—O) on the other are identical with those indicated by Thomas. The points P and O on the diagram are invariant, the point P being a eutectic of melting point 1320°, and point O a reaction point, melting point 1280°. When the limits of the field of solid solutions in the ternary system had been defined, the optical properties of the glasses and separated crystals were examined.

The results of the quenching of the samples investigated, with indications of the liquidus temperature, the nature of the primary phase, and the refractive indices of the glass, are given in the table.

The results of the optical investigation of the glasses showed that with increase in the contents of alumina and barium oxide the refractive index increases, and with increase in the silica content it diminishes. The refractive index of crystals of solid solution formed from the barium silicates $2BaO \cdot 3SiO_2$ and $BaO \cdot 2SiO_2$ at a constant alumina content changes as the ratio of the amounts of these silicates changes, diminishing from $2BaO \cdot 3SiO_2$ to $BaO \cdot 2SiO_2$. Reduction in the refractive index is observed also for a constant ratio of the silicates, but increasing amounts of silica (Fig. 2). This is characterized by reduction in the birefringence of the crystals.

In the field studied, therefore, we find changes in optical properties along two directions: along lines parallel to the side $BaO—SiO_2$, and along lines passing from this side to the central part of the triangle. Such a change in the optical properties of the crystals separating can be explained only on the assumption that they are formed from three components. Change in the refractive indices of the primary phases, in their dependence on composition, are shown graphically in Figures 2 (a) and 2 (b). In Fig. 2 (a), the variation of the index n_g with composition is shown, and in Fig. 2 (b) —the change of n_p with composition. The refractive indices for $BaO \cdot 2SiO_2$ and $BaO \cdot SiO_2$ are constant, and are represented by horizontal lines.

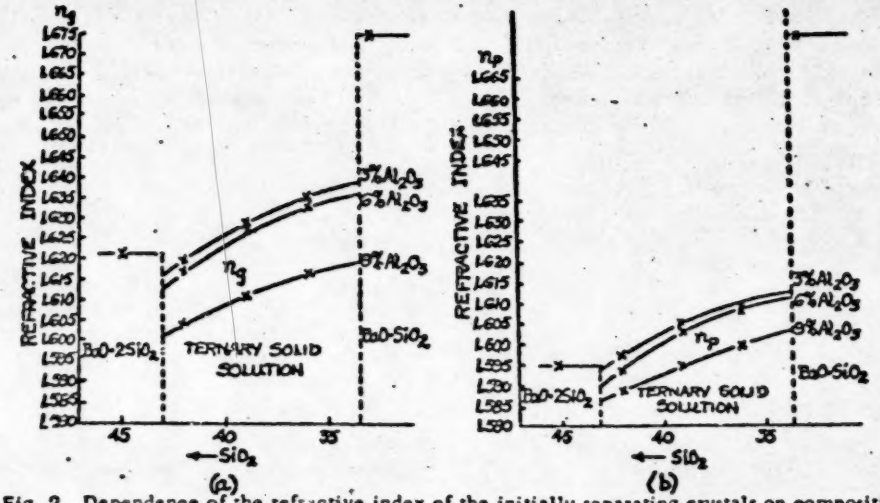

Fig. 2. Dependence of the refractive index of the initially separating crystals on composition for sections of constant alumina content (3, 6 and 9%): a) change in n_g; b) change in n_p.

The microscopy results are presented in the microphotographs in Figures 3-12.* Fig. 3 shows crystals of barium disilicate. The microstructures of ternary solid solutions containing 3 and 6% Al_2O_3 at different temperatures are shown in Figures 4-8: reduction in the temperature from which quenching occurs leads to increased tendency to crystallize and to separation of crystals in the form of fine grains with preservation of homogeneity. The crystallization of a solid solution with simultaneous formation of rectangular plates and needles of celsian having feeble birefringence is shown in Figures 9 and 12 (the photograph in Fig. 12 was obtained with a combined section in reflected light). Rounded grains of barium metasilicate in glass and elongated plates of solid solution are shown in Fig. 10.

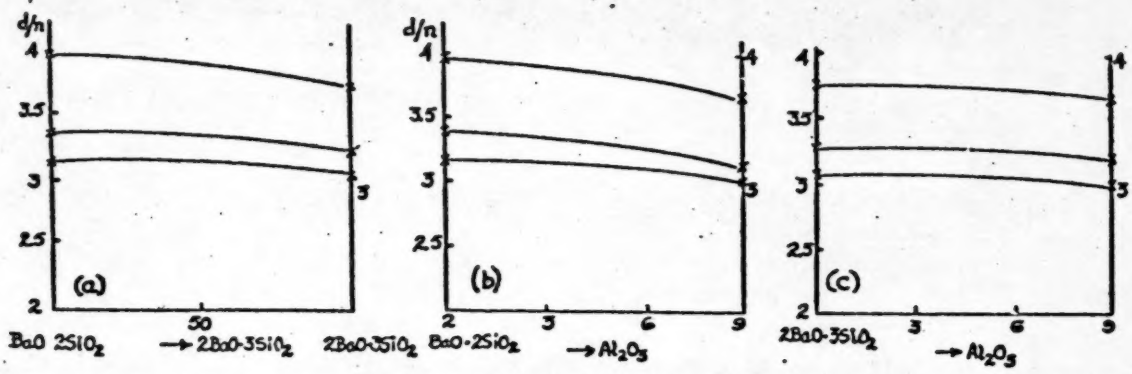

Fig. 13 (a, b and c). Dependence of the interplanar distances on the composition.

An X-ray investigation provided confirmation of the formation of ternary solid solutions; it was carried out with the aid of Co and K α,β radiation in cylindrical cameras, 57.3 mm in effective diameter. Increase both in the alumina content and also in the barium disilicate content caused a displacement of the lines in the X-ray picture with respect to those of the original sample of $2BaO \cdot 3SiO_2$, which is to be explained by the formation of a ternary solid solution of the replacement type.

* Figures 3-12 are to be found on the plate, page

Fig. 13 shows the dependence of the interplanar distances (d/n) of various samples on composition: Fig. 13 (a) gives the dependence for the series $BaO \cdot 2SiO_2 - 2BaO \cdot SiO_2$; Fig. 13 (b) for $BaO \cdot SiO_2$ with additions of 3, 6 and 9% Al_2O_3; Fig. 13 (c) for $2BaO \cdot 3SiO_2$ with additions of 3, 6 and 9% Al_2O_3. As will be seen from these figures, additions of $BaO \cdot 2SiO_2$ and $2BaO \cdot 3SiO_2$ result in increase in the value of d/n; inuroduction of alumina reduces the value of d/n, both for $BaO \cdot 2SiO_2$, and for $2BaO \cdot 3SiO_2$. The results of the investigation show that the field contiguous with the line of binary solid solution of the system $BaO - SiO_2$ consists of ternary solid solutions $2BaO \cdot 3SiO_2 - BaO \cdot 2SiO_2 - BaO \cdot Al_2O_3 \cdot 2SiO_2$.

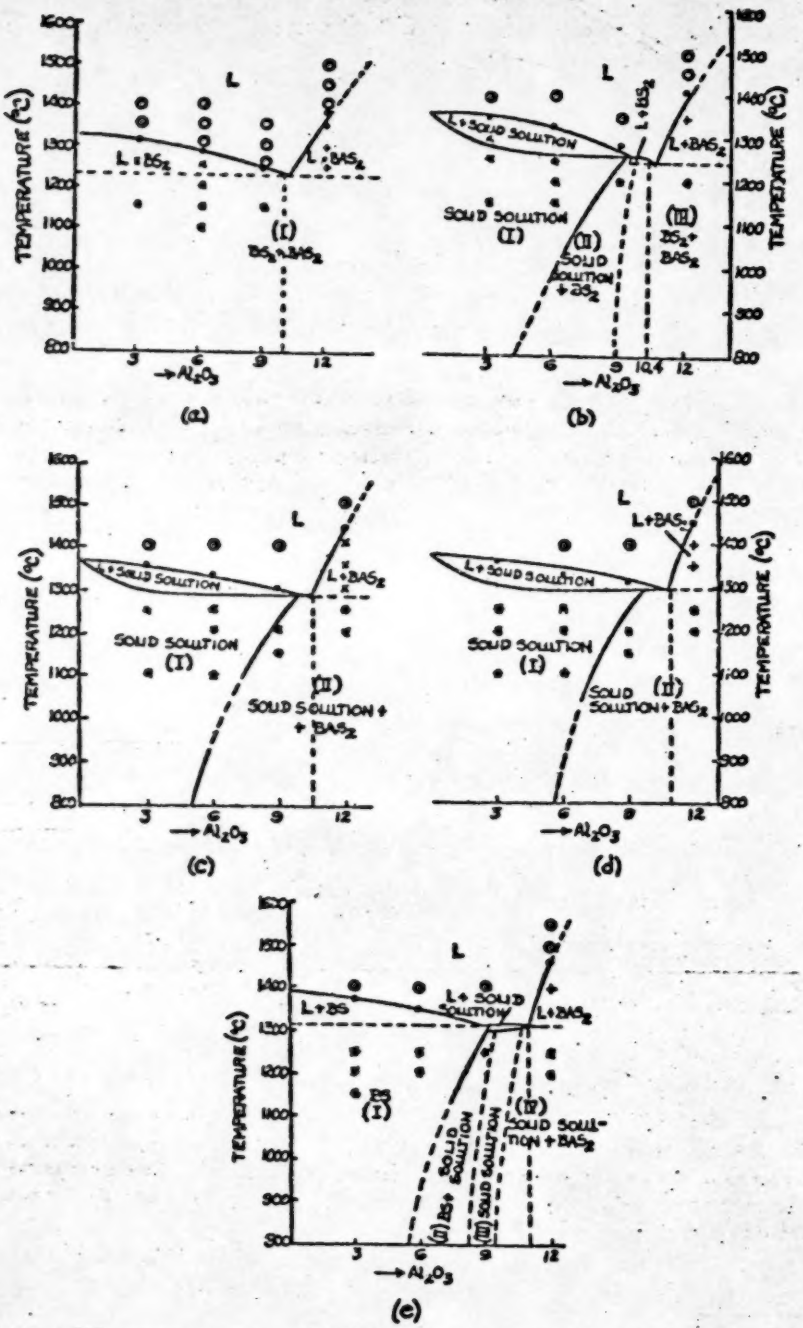

Fig. 14. Constant SiO_2 content sections: a) 45%; b) 42%; c) 39%; d) 36%; e) 33%.

On the basis of the results we have constructed vertical sections parallel to the side $BaO-Al_2O_3$, i.e., sections for constant silica contents of 45, 42, 39, 36 and 33%. The section for 45% SiO_2 [Fig. 14 (a)] passes across the field of barium disilicate and celsian and is a eutectic section. The eutectic corresponds to the simultaneous separation of $BaO \cdot 2SiO_2$ and $BaO \cdot Al_2O_3 \cdot 2SiO_2$ (I). The section for 42% SiO_2 [Fig. 14 (b)] intersects the field of solid solution, barium disilicate, and celsian. The field of existence of solid solution extends within fairly wide limits, and its extent is reduced as the temperature falls (I). A small two-phase region is to be noted; it consists of solid solution and barium disilicate (II). A eutectic is formed between barium disilicate and celsian (III).

The sections for 39 and 36% SiO_2 [Figures 14 (c) and (d)] have much in common: in each case the primary phases are solid solution and celsian. The limits of solid solution are narrowed as the temperature is lowered (I). The eutectic corresponds to the separation of solid solution and celsian (II). The difference between these two sections consists only in the crystallization temperatures of the separate components.

The section for 33% SiO_2 [Fig. 14 (e)] passes across the field of existence of barium metasilicate, solid solution, and celsian. The main field is that of barium metasilicate (I). The field of solid solution occupies a fairly narrow strip (III). Between $BaO \cdot SiO_2$ and the solid solution, a two-phase region exists: this consists of barium metasilicate and solid solution (II). A mixture of the eutectic type is formed between the solid solution and celsian (IV).

SUMMARY

1. It has been established that there is a field of ternary solid solutions formed by barium disilicate, dibarium trisilicate, and celsian, and its boundaries have been defined.

2. The refractive index for this region falls with increase in the contents of barium disilicate and alumina.

3. Five polythermal sections for constant silica contents of 45, 42, 39, 36 and 33% have been constructed; these enable the equilibrium relations to be characterized for the field studied.

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Institute of Silicate Chemistry of the USSR
Academy of Sciences

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ADSORPTION OF VAPOR AT A MERCURY SURFACE

COMMUNICATION 1

B. P. Bering and K. A. Iolleva

The study of the adsorption of gases and vapors at smooth homogeneous solid or liquid surfaces is very important for the elucidation of questions of fundamental significance in the theory of physical adsorption. In these cases the study of adsorption phenomena can be carried out under the cleanest possible conditions, without complications due to the geometric and energetic heterogeneity that is characteristic of the surfaces of technically important sorbents, and without the possibility of capillary condensation in fine pores. Such investigations can considerably extend our concepts of the energetic peculiarities and mechanism of the adsorptionprocess, of the properties of matter in the two-dimensional state, of the phase changes in the adsorption layer, and of the nature of the interaction between the adsorbed molecules. The use of crystalline solids for this purpose cannot completely remove the energetic heterogeneity of the surface, for the adsorption potential depends on the indices of the surfaces of the crystal, on the presence of apexes, edges, and cracks, and also on lattice defects on the surface of the crystal. Also, highly dispersed nonporous crystalline powders are systems having a secondary porosity due to the presence of gaps between the particles in which, at high relative pressures, capillary condensation may occur (at the points of contact of the particles.

On account of these considerations, a liquid mercury surface is of particular interest for the study of the adsorption of the vapors of substances that are insoluble in mercury. In this case, however, direct methods of measuring adsorption are of low accuracy, and much more reliable results can be obtained by an indirect method based on the measurement of the surface tension of mercury in the vapor of the substance concerned, followed by calculation of the amount of adsorption from the Gibbs equation. This method has been applied by a number of authors, but only in the work of Cassel and Salditt [1] and Cassel [2] has the first serious attempt been made to make a systematic study of the adsorption of polar and nonpolar substances on mercury. These investigations enabled the existence of two types of surface-pressure isotherms (and the corresponding adsorption isotherms) to be established. Nonpolar substances give convex surface-pressure isotherms, corresponding to Type I (or II) in Brunauer's classification of adsorption isotherms [3]; surface-pressure isotherms for water and the lower alcohols are concave at low relative pressures and correspond to Type III (or V) adsorption isotherms in the same classification.

Kemball and Rideal [4] and Kemball [5] have recently published a series of investigations in which they have repeated the determinations of Cassel and Salditt by the method based on the measuring of a recumbent drop. As a result of careful experiments, they have shown that all of the substances studied (including water and the lower alcohols) give convex adsorption isotherms, which can be described in the monomolecular region by Volmer's equation. They explain the concave isotherms of Cassel by the presence of contamination, which causes the values found for the surface tension of mercury to be too low.

In 1940, one of the authors of this paper carried out measurements of the surface tension of mercury in water vapor, ethyl alcohol, and butyl alcohol by the method based on the determination of the maximum pressure in drops, and the isotherms obtained for these substances were of Types III and V. Kemball's results conflict markedly with the results of this investigation, and we, therefore, decided to repeat the measurements on the adsorption of a number of substances on mercury by the maximum drop-pressure method. The experimental side of this investigation has been described in detail in our preliminary communication [6].

EXPERIMENTAL RESULTS

The measurement of adsorption by the method under consideration makes very stringent demands with respect to the cleaniness of the mercury surface, and hence, in the judging of the reliability of such measurements, particularly important parts are played by the value of the surface tension of pure mercury and the temperature coefficient of this quantity. The surface tension of mercury was measured in a vacuum in the temperature range 15-96°, and in this range the values obtained can be represented, accurate within $\pm$ 0.2%, by the following equation:

$$\sigma_t = 489.5 - 0.20\,t \qquad (1)$$

The value σ_0 = 484.5 dyne/cm at 25° is in excellent agreement with the value σ_0 = 484.2 ± 0.5 dyne/cm, obtained at the same temperature by Kemball. The value we obtained for $d\sigma_0/dt = -0.20$ agrees exactly with the value obtained by Kemball.

When we had obtained constantly reproducible values of σ_0 we carried out several series of measurements of the surface tension σ in the vapors of water, methanol, acetone, diethyl ether, and heptane at 15, 25, and 40° and at various pressures. In the table we give the values of the surface pressure $\pi = \sigma_0 - \sigma$ and the corresponding values of the relative pressure $h = p/p_0$ for water and methanol. Our experimental results for other substances, and their discussion, will be given in the second communication of this series.

t°	h·10²	π	h·10²	π	h·10²	π	h·10²	π	h·10²	π
1	2	3	4	5	6	7	8	9	10	11
Water										
At t = 15° p_0 = 12.79 mm Hg; at t = 25° p_0 = 23.76 mm Hg										
15	38.6	0.0	51.7	1.6	66.5	7.6	81.5	13.7	95.5	21.4
	39.8	0.2	52.6	2.4	68.5	8.6	83.5	14.9	95.5	21.9
	40.0	0.0	54.0	2.7	70.0	9.0	86.0	15.9	98.5	23.7
	44.5	0.5	56.5	3.2	74.0	10.2	86.5	16.8	99.0	23.9
	46.5	0.4	59.5	4.3	75.0	11.0	89.0	17.5	100.0	31.0
	48.4	0.5	62.0	4.1	76.1	12.4	90.5	18.1	100.0	30.8
	49.1	0.8	64.0	6.0	79.5	13.4	91.5	18.5		
	50.5	1.8	64.8	6.6	79.5	12.5	91.5	18.3		
25	30.0	0.1	59.0	3.7	69.5	7.3	82.5	12.8	95.6	22.4
	47.5	0.0	59.0	3.1	71.0	7.3	84.0	12.6	96.5	22.7
	49.0	0.7	60.5	4.1	72.0	8.1	87.6	13.9	98.0	25.5
	52.5	0.6	61.5	5.1	75.0	9.0	89.0	15.3	99.0	27.2
	54.0	2.0	63.0	4.7	77.5	11.2	90.0	16.0		
	56.5	3.2	65.0	6.3	78.6	11.7	94.1	18.8		
	57.0	2.3	66.0	6.3	79.5	12.0	94.5	18.7		
Methanol										
At t = 15° p_0 = 72.0; at t = 25° p_0 = 123.0; at t = 40° p_0 = 280.0 mm Hg										
15	4.20	0.0	32.7	10.0	59.1	28.4	67.2	34.5	90.4	55.1
	9.70	0.7	41.7	16.3	59.7	29.3	71.0	38.3	90.4	54.9
	12.5	0.9	50.0	21.9	61.2	30.5	71.5	38.1	94.5	61.5
	16.7	1.9	55.6	25.6	62.6	31.6	82.0	47.8	94.5	62.3
	19.5	3.4	56.3	26.1	63.2	31.3	84.0	49.1	100.0	79.1
25	1.10	0.0	10.7	0.7	23.6	4.3	45.0	17.7	78.0	44.1
	2.50	0.0	15.0	1.3	24.8	5.0	49.6	20.2	85.5	50.1
	3.30	0.3	16.3	1.5	31.0	8.1	59.4	27.7	90.5	54.7
	3.90	0.4	18.2	2.1	34.2	10.2	63.5	31.0	98.0	70.0
	9.03	0.5	22.0	3.7	40.7	14.5	66.7	33.8	99.8	81.5
40	1.05	0.0	6.30	0.2	15.1	1.1	21.4	3.0	30.6	7.3
	1.25	0.0	7.60	0.3	16.6	1.2	22.2	3.5	34.7	9.7
	2.32	0.0	10.0	0.5	17.3	1.3	22.8	3.6	38.0	12.0
	4.50	0.0	11.9	0.6	18.0	1.3	25.8	4.8	39.2	12.5
	5.40	0.2	13.2	0.8	19.8	2.3	28.0	5.5	40.9	13.1

In order to calculate the adsorption from the surface-pressure isotherms $\pi = \pi(h)$, the experimental results were expressed in the coordinates (π, log h), and graphical differentiation of the smooth curves drawn through the experimental points yielded values of the adsorption Γ according to the Gibbs equation $\Gamma = (1/kT)(d\pi/d \ln h)_T$ at various values of h. The calculated values of Γ were represented in the coordinates (Γ, log h), and smooth curves were drawn through the points obtained, after which the adsorption isotherms were presented in the usual coordinates (Γ, h).

This method of calculating the adsorption isotherms is very convenient, and it results in a minimum of subjective errors.

In calculations of adsorption from the experimental curves $\pi = \pi(\log h)$, the question of the accuracy of such calculations arises. It appears that in the general case it is impossible to find the value of the possible error in a derivative when the probable error of discrete values of the function is known. The possibility exists, however, of verifying the correctness of the calculation of the derivative by numerical integration of the derivative function and comparison of the calculated values of the function with the measured values. In our case, in order to check the resulting adsorption isotherms we calculated back from the curves $\Gamma = \Gamma(\log h)$ in order to obtain the isotherms $\pi = \pi(\log h)$ (by integration of the Gibbs equation). With this object, by measurement of the area under the curve $\Gamma = \Gamma(\log h)$ in the interval from h_1 to h_2 we determined the value of $\Delta\pi = kT \int_{h_1}^{h_2} \Gamma d \ln h$, the integration being carried out from the lower limit h_1, corresponding to the maximum measured value π_{max}. The difference $\pi_{max} - \pi$ was represented graphically as a function of h and compared with the experimental values of π.

This check, which was carried out for all of the substances studied, gave close agreement between calculated and measured values of π. We give Fig. 1 as an illustration. On this graph the experimental values of π for heptane at 25° are marked by circles, and first of all a smooth curve was drawn through these points. Graphical differentiation of this curve yielded the adsorption isotherm (Curve 2 in Fig. 1). The result of the integration of this curve is

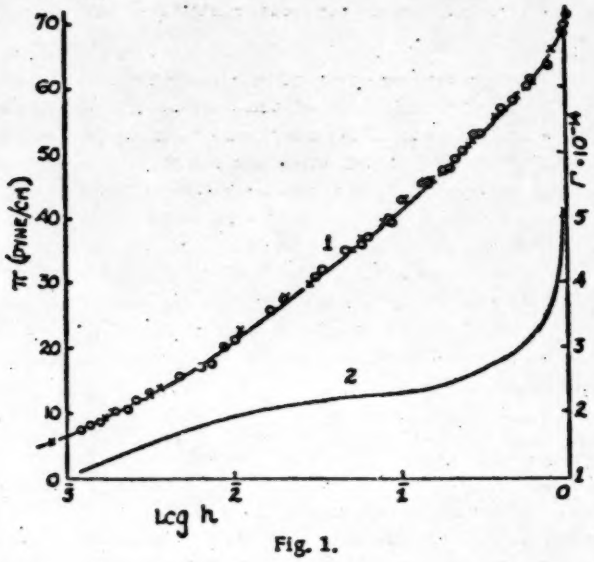

Fig. 1.

represented by the continuous curve 1. As Fig. 1 shows, the experimental points fit very well to Curve 1. This circumstance makes it very probable that the calculated adsorption isotherm corresponds precisely to the experimentally found curve $\pi = \pi(\log h)$.

Fig. 2 gives the isotherms $\pi = \pi(\log h)$ for water at 15° (Curve 1) and for methanol at 40° (Curve 2). On the same graph there are shown also the corresponding curves for ethyl alcohol at 20° (Curve 3) and butyl alcohol at 50° (Curve 4), which were obtained previously by one of the authors of this paper. At that time the corresponding measurements for water were not completed, but, in this case also, an appreciable fall in σ in water vapor was observed only for $h > 0.5$, and a concave isotherm $\pi = \pi(h)$ was obtained. It is possible that the lower value of σ_0 found in these experiments (471.0 dyne/cm at 25°) was the result of a systematic error. The values of π for ethyl and butyl alcohols have been increased by 2.7% in Fig. 2, and so adjusted to the value $\sigma_{25°} = 484.5$ dyne/cm.

DISCUSSION OF EXPERIMENTAL RESULTS

It is first necessary to point out the close agreement between the curves $\pi = \pi(\log h)$ obtained by us and the corresponding curves obtained by Kemball for heptane and acetone. In Fig. 1 the crosses indicate the values of π found by Kemball for heptane at 25°. Equally close agreement is observed also for acetone at 25°. This fact is in

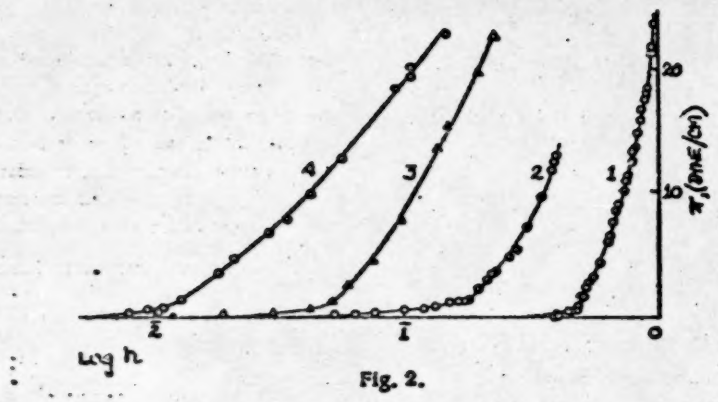

Fig. 2.

itself deserving of attention, since for the first time, in two series of completely independent measurements carried out in different laboratories by different methods, complete agreement has been obtained, not only with respect to the absolute values of σ_0 and $d\sigma_0/dt$, but also with respect to the surface-pressure isotherms, and, therefore, the adsorption isotherms of the two substances on mercury. These facts make it all the more surprising that there should be such a notable qualitative divergence between our measurements and those of Kemball in the case of water and alcohols.

In Fig. 3 we give the curves $\pi = \pi(p)$ for water at 25°, both according to Kemball's results (Curve 1), and also according to our results (Curve 2). We consider that, of these curves, only Curve 2 corresponds to the physical adsorption of water vapor on mercury. The crucial point is that in the method of maximum pressure the time for the formation of the drop does not exceed 2-3 minutes, whereas in the method used by Kemball the mercury surface remains for a long time (throughout the whole series of measurements) in contact with the atmosphere of vapor in the apparatus. It, therefore, seems possible to us that the much greater reduction in σ in Kemball's experiments is due to one of two causes. In the first place, the possibility is not excluded that water and alcohols, being adsorbed on the glass of the apparatus, displace some substances from the glass, which are then adsorbed on the mercury surface and cause increase in the values of π. In this connection we may point out that we have observed that when the apparatus has not been cleaned with sufficient care the values of σ gradually fall at constant water vapor pressure. In this case, the values of π were found to be higher than those found later, after longer evacuation with intermediate "washing" of the apparatus with water vapor. The second cause of the divergence could be the occurrence of slow processes of the activated-adsorption type, which could become manifest in the static method of Kemball, but not in the maximum pressure method.

However, whichever of these explanations may be true, we consider that, for water and alcohols, our measurements are correct, and those of Kemball are incorrect. The main objection advanced by Kemball against the concave surface-pressure isotherms in Cassel and Salditt's paper was based on the low vacuum value of σ_0 (455 dyne/cm at 50°), which Kemball ascribed to the presence of surface-active contamination. It will be clear that this objection cannot be applied to our measurements.

The recently published paper of Karpachev, Smirnov, and Volchenkova [7] has convinced us still more of the incorrectness of Kemball's measurements. In this paper, the authors, without burdening themselves with references to the literature, have described a copy they have made of Kemball's apparatus (in a considerably worsened variant) and have given results of measurements of the surface tension of mercury in a vacuum (σ_0 = 477.4 dyne/cm at 30°) and in water vapor. Curve 3 in Fig. 3 shows their isotherm $\pi = \pi(p)$ at 30°. Curves 1 and 3 in this figure are far from coincident, although the values of σ_0 are close. In our opinion, this means that neither of these curves has any relation to the physical adsorption of water vapor on the surface of mercury.

Passing to an examination of our results, we will first consider the adsorption isotherms for alcohols and water calculated on the basis of the curves in Fig. 2. Fig. 4 shows the adsorption isotherms for water at 15° (Curve 1), methyl alcohol at 40° (Curve 2), ethyl alcohol at 20°(Curve 3), and butyl alcohol at 50° (Curve 4). For each of these substances, there is a sudden jump in adsorption at constant h, which is characteristic for a two-dimensional phase transition of the first kind, corresponding to two-dimensional condensation. In this connection we must point out that, as a more careful examination of the results of our measurements has shown, the conclusions reached in our preliminary communication [6] regarding the absence of vertical jumps in the adsorption isotherms is erroneous.

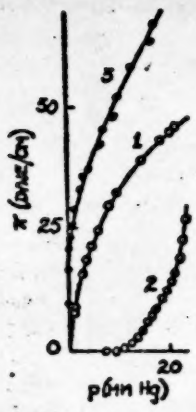

Fig. 3

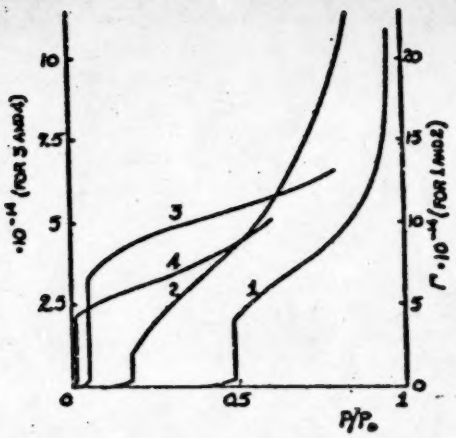

Fig. 4

In 1925 Frumkin showed for the first time [8] that the occurrence of two-dimensional condensation will be indicated by a break in the surface-pressure isotherm. In the work cited such a break was found in the isotherm for the surface pressure of aqueous solutions of lauric acid. On the curves $\pi = \pi(\log \underline{h})$ in Fig. 2, distinct breaks can be seen for water and methyl alcohol, the breaks for ethyl and butyl alcohols being less distinct, probably owing to the lower number of experimental points. For the water and methyl alcohol isotherms, the breaks are still present at the other temperatures studied. There is little room for doubt, therefore, that two-dimensional condensation occurs in the physical adsorption of water and lower aliphatic alcohols on mercury in the temperature range 15-40°.

As is well-known, the adsorption isotherms for water and methyl alcohol at graphite and nonporous carbon black surfaces [9] are very similar in form to the isotherm represented by Curve 1 in Fig. 4. It may be considered that this resemblance is due to the identity of the mechanisms in the two cases. The absence of a vertical jump in the adsorption isotherms for water vapor at carbon adsorbents probably arises from surface heterogeneity. Curve 1, Fig. 4, therefore, may be regarded as a confirmation of the correctness of the views on the nature of the adsorption of water vapor on carbon that have been advanced by Dubinin in a number of papers [10].

Comparatively recently phase transitions of the first kind have been found by Harkins and coworkers [11] in the study of the adsorption of heptane on silver, ferric oxide, and graphite. However, careful verification has shown that in the adsorption of heptane on silver [12], and on ferric oxide and graphite [13] no signs of two-dimensional condensation can be detected. It thus appears that only in the work of Clark and Ross [14] has two-dimensional condensation been actually observed (for ethane on sodium chloride). In this connection, the fact that we have established the absence of a first-order phase transition in the adsorption of heptane on mercury may be regarded as further confirmation of the incorrectness of the results of Harkins and coworkers [11].

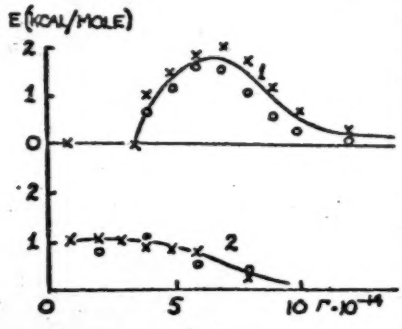

Fig. 5.

On the basis of our results we can make a rough estimate of the value of the two-dimensional pressure π_c at which two-dimensional condensation occurs. The resulting values of π_c for water, methyl alcohol, ethyl alcohol, and butyl alcohol are 0.8, 1.3, 1.0, and 0.8 dyne/cm, respectively. According to Adam [15], for pentadecanoic acid on water $\pi_c = 0.1$ dyne/cm, and with reduction in the length of the carbon chain, the pressure π_c rises by approximately 0.1 dyne/cm for each carbon atom removed. If we assume that this relationship is valid also for aliphatic alcohols, then the results of our evaluation of π_c are in accord with these observations.

The accuracy of the measurement of π is insufficient and the temperature range of the measurements is too small to permit the determination of the two-dimensional critical temperature for the substances investigated. As Devonshire [16] has shown from statistical considerations, for the very simple case of the adsorption of the inert gases the ratio of the two-dimensional critical temperature T'_k to the three-dimensional critical temperature is $T'_k/T_k = 0.53$. This ratio, however, depends on

the individual properties of the molecules and on their interaction in the adsorption layer. We have observed the phenomenon of two-dimensional condensation on mercury only for substances that associate in the condensed phase under the action of hydrogen bonds, and it may, therefore, be supposed that this form of attractional interaction increases the probability of two-dimensional condensation, other things being equal, and will, therefore, lead to an increase in T'_k relative to 0.53 T_k. For the alcohols studied $T'_k/T_k > 0.58$. The presence of induced dipole moments must tend to prevent two-dimensional condensation and lower T'_k. For heptane (T_k = 540° K) at 15° two-dimensional condensation does not occur, and therefore, $T'_k/T_k < 0.53$. Though having nearly the same critical temperature, acetone (T_k = 508°), unlike ethyl alcohol (T_k = 517°), does not exhibit two-dimensional condensation. A similar picture is to be observed for benzene (T_k = 564°) (according to Kemball's results) and butyl alcohol (T_k = 560°).

In Fig. 5 we give curves for the dependence of the differential heat of adsorption q on the value of the adsorption Γ, calculated from the 15° and 25° isotherms for water (Curve 1) and the 25° and 40° isotherms for methyl alcohol (Curve 2). In Fig. 5 the ordinates represent the "pure" heat of adsorption $E = q - \lambda$, λ being the heat of condensation. For water the curve $E = E(\Gamma)$ passes through a maximum, which occurs at a coverage $\theta \approx 1$, and which approaches the axis of abscissa as Γ becomes still greater. It appears that the heat of two-dimensional condensation is almost equal to the heat of condensation λ, for in the range of values corresponding to two-dimensional condensation, E is close to zero. Curve 2 in the same figure represents the corresponding relationship $E = E(\Gamma)$ for methyl alcohol. In this case, E has no distinct maximum and gradually falls to zero. The heat of two-dimensional condensation exceeds λ by about 1 kcal/mole.

The calculation of E for water and methyl alcohol was carried out in the first place by the Clausius-Clapeyron equation $E = RT^2(d\ln h/dT)_\Gamma$, and in the second place by the Williams equation [17]:

$$E = \frac{d}{d\Gamma}\left[\pi - T\left(\frac{d\pi}{dT}\right)_h\right] \qquad (2)$$

directly from two $\pi = \pi(\log h)$ isotherms corresponding to two different temperatures. The results of the calculation by the first method are denoted in Fig. 5 by crosses, and those obtained by the second method, by circles. The difference in the calculated values of E gives an idea of the possible calculation error.

The authors are greatly indebted to V. V. Serpinsky, M. M. Dubinin, and B. V. Ilyin for their interest in the work and valuable advice.

SUMMARY

1. By a method based on the maximum pressure in a drop, measurements have been made of the surface tension of mercury in a vacuum, in water vapor, and in methanol vapor. In the temperature range 15-96° the surface tension of mercury is expressed by the formula $\sigma = 489.5 - 0.20t$.

2. On the basis of these measurements, adsorption isotherms have been calculated for the vapors of these substances on mercury. The previously obtained adsorption isotherms for ethyl and butyl alcohols are also given.

3. In the adsorption of water and alcohols on mercury, a first-order two-dimensional phase transition has been observed, corresponding to two-dimensional condensation. It has been shown that the results of analogous measurements by Kemball for water and alcohols are incorrect.

4. In the case of water, the heat of two-dimensional condensation appears to be close in value to the usual heat of condensation, but in the case of methanol the former exceeds the latter by 1 kcal per mole.

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Institute of Physical Chemistry of the
USSR Academy of Sciences

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SYSTEMS CONTAINING HYDROGEN PEROXIDE AT HIGH CONCENTRATION

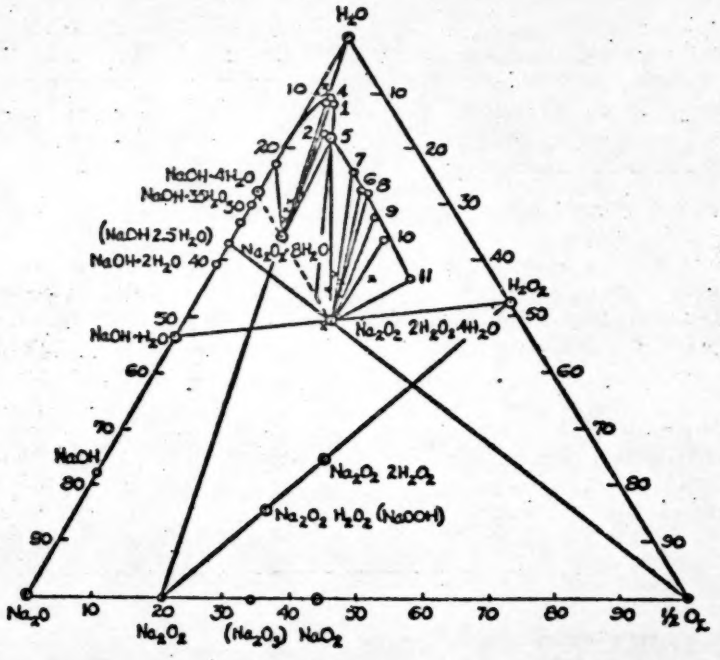
COMMUNICATION 7. 0° ISOTHERM OF THE TERNARY SYSTEM $NaOH-H_2O_2-H_2O$

S. Z. Makarov and N. K. Grigoryeva

The investigation of the ternary system $NaOH-H_2O_2-H_2O$ by the solubility method was undertaken in connection with the study of a number of questions relating to the interaction of hydrogen peroxide solutions and the hydroxides of alkali and alkaline-earth metals. These reactions, as our investigations have shown, are accompanied not only by the formation of hydrated forms of the peroxide compounds of the metals, but also, at higher hydrogen peroxide concentrations, by the formation of perhydrates – products of the addition of H_2O_2, and possibly compounds of the so-called hydroperoxide type. It should be noted that a completely clear picture of the nature of these substances is not yet to be found in the literature, and for this reason the most diverse ideas are to be found concerning the structure of the so-called hydroperoxides, in spite of the large number of investigations that were made in the period 1662-1912.

Of these investigations, the most significant are those of Harcourt [1], Schöne [2], Tafel [3], D'Ans and Friedrich [4], Wolffenstein and Peltner [5], and Pisarzhevsky [6]. For the hydroperoxide compounds of sodium the following forms have been indicated: 1. NaOOH or $Na_2O_2 \cdot H_2O_2$; 2. $NaOOH \cdot 0.5H_2O_2$ or $Na_2O_2 \cdot 2H_2O_2$; 3. $NaOOH \cdot 0.5H_2O_2 \cdot 2H_2O$ or $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$. The sodium peroxide hydrates indicated were: 1. $Na_2O_2 \cdot 8H_2O$, the octahydrate; 2. $Na_2O_2 \cdot 2H_2O$, the dihydrate; 3. $Na_2O_2 \cdot H_2O$, the monohydrate.

If we start from the simplest concepts concerning normal peroxide compounds as products of the replacement of hydrogen in the H_2O_2 molecule by metal, we can obviously have only two kinds of compounds: M–OOH and M–O–O–M, i.e., M_2O_2 – the so-called hydroperoxides and peroxides. These compounds may become more complicated by the addition of molecules of H_2O and H_2O_2. It will be clear that for the final solution of the question of the actual structures of these compounds, special investigations directed to the determination of these structures must be carried out.



TABLE

Data Relating to 0° Isotherms

Point No.	Composition of original medium	Composition of the liquid phase (% by wt.)				Composition of residue (% by wt.)			Solid phase
		active O_2	Na_2O	H_2O	$\frac{O_2}{Na_2O}$	active O_2	Na_2O	H_2O	$\frac{O_2}{Na_2O}$	
3	25% NaOH + 56% H_2O_2	2.84	9.18	87.98	0.309	6.31	26.21	67.48	0.240	$Na_2O_2 \cdot 8H_2O$
4	25% NaOH + 72% H_2O_2	2.88	8.30	88.82	0.347	5.94	25.06	69.00	0.236	The same
1	25% NaOH + 20% H_2O_2	3.14	8.78	88.06	0.357	5.59	23.31	71.10	0.239	"
2	25% NaOH + 30% H_2O_2	4.81	12.41	82.78	0.387	6.11	21.61	72.28	0.281	"
5	$Na_2O_2 \cdot 8H_2O$ + 30% H_2O_2	6.45	11.54	82.01	0.553	14.64	23.85	61.51	0.613	$Na_2O_2 \cdot 8H_2O$ + + $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$
7	$Na_2O_2 \cdot 8H_2O$ + 80% H_2O_2	12.67	11.20	76.05	1.123	18.78	26.57	54.65	0.706	$Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$
6	$Na_2O_2 \cdot 8H_2O$ + 72% H_2O_2	15.31	12.28	72.41	1.246	18.85	23.78	57.37	0.792	The same
8	$Na_2O_2 \cdot 8H_2O$ + 88% H_2O_2	16.24	11.33	72.43	1.430	20.32	23.33	56.35	0.874	"
9	NaOOH + 65% H_2O_2	19.75	12.14	67.81	1.580	20.30	25.20	54.50	0.805	"
10	NaOOH + 88% H_2O_2	22.62	13.66	63.72	1.650	21.17	30.39	48.44	0.696	"
11	NaOOH + 93% H_2O_2	30.74	12.90	56.36	-	24.61	18.30	57.09	-	"

EXPERIMENTAL

At first it was proposed to study isotherms for above 0°, but it was found that under these conditions rapid decomposition reactions occur, so that it is more expedient to study isotherms for the system $NaOH-H_2O_2-H_2O$ at low temperatures. The investigation of the 0° isotherm was carried out in a thermostat in which the constant temperature was maintained by means of ice or snow.

The initial reactants were NaOH solutions of various concentrations and hydrogen peroxide solutions, free from stabilizers, and again of various concentrations. It was established by preliminary experiments that it was not desirable to use very strong NaOH solutions, since the reaction between NaOH and H_2O_2 yielded much heat and resulted in large losses of oxygen. The most suitable NaOH concentration was found to be about 25-30%.

Active oxygen was determined by a permanganate method, as follows: a sample of the liquid phase or residue was transferred to a weighed beaker containing boric acid, and the sample was dissolved in cooled water and titrated with potassium permanganate in presence of sulfuric acid. The determination of Na_2O was carried out as follows: the weighed amount of liquid phase or residue was dissolved in water in an Erlenmeyer flask and boiled for 1-2 hours until completely decomposed; the solution was then cooled and titrated with hydrochloric acid.

When a 25% NaOH solution interacted with 20%, 30%, 56%, and 72% hydrogen peroxide, the residue of crystals obtained was close in composition to sodium peroxide octahydrate $Na_2O_2 \cdot 8H_2O$. The results of these experiments are given in the table and in the solubility diagram, which represents the system $Na_2O-H_2O-0.5O_2$ on a Gibbs triangle. It follows from the results given in the table and in the diagram that the interaction of NaOH and H_2O_2 yields $Na_2O_2 \cdot 8H_2O$.

When crystals of $Na_2O_2 \cdot 8H_2O$ reacted with 30%, 72%, 80% and 88% hydrogen peroxide at 0°, a compound was obtained that was close in composition to

the so-called "hydroperoxide" $NaOOH \cdot 0.5H_2O_2 \cdot 2H_2O$ (or $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$). In spite of further increase in the concentration of H_2O_2 in the liquid phase at this temperature, no compounds richer in oxygen were obtained.

When the crystals obtained as above were immediately treated with a new portion of 65% or 88% H_2O_2, only the original phases were obtained. When the crystals of "sodium hydroperoxide" were treated with 93% hydrogen peroxide, a residue was obtained that rapidly began to decompose. The solubility diagram that we obtained for the 0° isotherm consists of two clearly defined branches corresponding to saturation with respect to the two solid phases $Na_2O_2 \cdot 8H_2O$, and $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$. The $NaOH \cdot 4H_2O$ branch is extremely small: the initial solubility of NaOH is 29.2%, the solid phase being $NaOH \cdot 4H_2O$. The limits of the existence of $Na_2O_2 \cdot 8H_2O$ are determined by the composition at the multiple point (No. 5 in the table). The limiting concentration attained by H_2O_2 in the liquid phase at 0° is about 65%, and the solid phases are then insufficiently stable and the residues readily decompose.

SUMMARY

1. The 0° isotherm of the system $NaOH-H_2O_2-H_2O$ has been studied for H_2O_2 contents of up to 65% in the liquid phase by the solubility method.

2. The presence of three solid phases has been established, their compositions being $NaOH \cdot 4H_2O$, $Na_2O_2 \cdot 8H_2O$, and $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$. The last phase, $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$, can be regarded also as a hydroperoxide of composition $NaOOH \cdot 0.5H_2O_2 \cdot 2H_2O$, but special investigation will be necessary to determine which is the actual form.

3. Sodium peroxide octahydrate $Na_2O_2 \cdot 8H_2O$ has been prepared in well-formed, platelike crystals, which are quite stable when kept in the cold. They are converted by dehydration into anhydrous sodium peroxide.

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N. S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences

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BABINET'S PRINCIPLE, AND THE LOW-ANGLE SCATTERING OF X-RAYS BY POROUS GLASSES

E. A. Porai-Koshits and V. N. Filipovich

The application of the method of low-angle X-ray scattering to the study of the structure of highly dispersed porous substances (gels, catalysts, porous glasses, etc.) meets with a number of specific difficulties associated not only with the variety of dimensions, form, and spatial distribution of the dispersed substance, but also with the applicability of the so-called Babinet's principle. Some authors, in determining the radii of the heterogeneous regions by this method, have associated them with the dimensions of the particles [1], whereas others have associated them with the dimensions of the pores [2]. In many cases, the problem of "pores or particles" has been solved by comparison of X-ray data with data obtained by other methods (electron microscope studies, sorption measurements, etc.), but owing to the relatively recent development of all these methods of studying the submicroscopic structure of materials full concurrence of results has been attained only in the simplest cases; generally, however, it has been shown that there is an absence of conflict between results obtained by different methods, but this, of course, is not a direct and unequivocal proof of a solution to this problem.

In the first part of this paper we examine the essential nature of Babinet's principle and its applicability to the scattering of X-rays at low angles. In the second part, we give the results of a special investigation directed to the solution of the problem of "pores or particles" for the case of porous glasses (preliminary studies of the structure of these glasses by the low-angle method have been described previously [3]).

1.

As is well-known [4], the intensity $I(\vec{s})$ of X-rays scattered by a specimen of volume V in the direction of the unit vector $\vec{s}$, may be expressed (under the conditions for Fraunhofer diffraction) in the following form:

$$I(\vec{s}) = \frac{I_0}{D^2}\left(\frac{e^2}{mc^2}\right)\frac{1+\cos^2 2\theta}{2}\left|\int_V \rho(\vec{r})e^{i(\vec{s}\vec{r})}dV\right|^2; \qquad (1)$$

(D is the distance from the specimen to the film; $\vec{s} = \frac{2\pi}{\lambda}(\vec{s}_1 - \vec{s}_0)$, in which λ is the wavelength; $\vec{s}_0$ is the unit vector in the direction of the incident parallel beam; $\theta = \frac{\vec{s}_1\vec{s}_0}{2}$, half of the scattering angle; and $\rho(\vec{r})$ is the electron density of the specimen). Dividing Equation 1 by the preintegral factor and keeping the same expression on the left hand side ($I(\vec{s})$), we have:

$$I(\vec{s}) = \left|\int_V \rho(\vec{r})\, e^{i(\vec{s}\vec{r})}\, dV\right|^2. \qquad (2)$$

The solution of this equation with respect to $\rho(\vec{r})$ forms the main problem of X-ray structure analysis.

Apart from purely mathematical difficulties in the satisfactory solution of Equation 2 (these depend on the nature of the scattering object, which may be a gas, crystal, liquid, or amorphous solid), there is one question of principle that makes the unequivocal determination of $\rho(\vec{r})$ from $I(\vec{s})$ practically impossible. The essential point is that generally $I(\vec{s})$ can be determined experimentally with sufficient accuracy only for scattering angles exceeding a certain small angle, the value of which depends on the setting and accuracy of adjustment of the apparatus; and in this connection particular importance must be attached to Babinet's principle, the essential nature of which will be clear from the following.

Let us express $\rho(\vec{r})$ in the form:

$$\rho(\vec{r}) = \bar{\rho}(\vec{r}) + \Delta\rho(\vec{r}), \qquad (3)$$

in which $\bar{\rho}(\vec{r})$ is the average electron density within the specimen:

$$\bar{\rho}(\vec{r}) = \frac{1}{V}\int \rho(\vec{r})\, dV$$

and is zero outside the specimen; $\Delta\rho(\vec{r})$ is the departure of the value of the electron density from the value $\bar{\rho}$.

From Equations 2 and 3 we obtain:

$$I(s) = \left|\int [\bar{\rho}(\vec{r}) + \Delta\rho(\vec{r})]\, e^{-i(\vec{s}\,\vec{r})}\, dV\right|^2 = \left|\int \bar{\rho}(\vec{r}) e^{i(\vec{s}\,\vec{r})}\, dV\right|^2 + 2\mathrm{Re}\int \bar{\rho}(\vec{r}_1) e^{i(\vec{s}\,\vec{r}_1)}\, dV_1 \int \Delta\rho^*(\vec{r}_2) e^{-i(\vec{s}\,\vec{r}_2)}\, dV_2 + \left|\int \Delta\rho(\vec{r}) e^{i(\vec{s}\,\vec{r})} dV\right|^2. \quad (4)$$

The first two terms in Equation 4 determine the so-called "zero-angle scattering"; they both contain, as a factor, the integral

$$\int \bar{\rho}(\vec{r}) e^{i(\vec{s}\,\vec{r})} dV, \quad (5)$$

corresponding to the amplitude of the scattering of an ideally homogeneous specimen, and therefore, differing from zero only for $s < s_0$, s_0 being a very small quantity; i.e., at very low scattering angles. We may point out that the evaluation of the value of s_0 so that for $s > s_0$ the zero-angle scattering can be neglected cannot be based on the Fraunhofer approximation for the usual experimental arrangement; the treatment must be based on Fresnel diffraction. Such an evaluation, however, is associated with further mathematical difficulties, and we shall not carry it out. The evaluation that we have given previously for scattering by a liquid [5] did not take this circumstance into account. As experiment shows, the values of s_0 are in any case very much lower than the values of s at which low-angle scattering is to be observed, even when the dimensions of the scattering particles are very great (of the order of 1000 A). This is evidenced by the existence of comparatively homogeneous materials (and they are in a majority) that do not give low-angle scattering even when exposures of hundreds of hours are given; although, of course, they show zero-angle scattering.

Let us examine now the intensity of the scattering $I'(\vec{s})$ by a specimen having an electron density $\rho'(\vec{r})$ such that

$$\rho'(\vec{r}) = \rho_0(\vec{r}) - \rho(\vec{r}) = \rho_0(\vec{r}) - \bar{\rho}(\vec{r}) - \Delta\rho(\vec{r}) = \bar{\rho}'(\vec{r}) - \Delta\rho(\vec{r}); \quad (6)$$

(in this equation $\rho_0(\vec{r})$ may be considered, within wide limits, to be an arbitrary constant inside the specimen, and equal to zero outside the specimen). It is obvious that, if we do not wish $\rho'(\vec{r})$ to have negative values, it is necessary that $\rho_0(\vec{r})$ within the specimen should not be less than the maximum value of $\rho(\vec{r})$. The value of $\rho'(\vec{r})$ is a maximum when that of $\rho(\vec{r})$ is a minimum (and vice versa), and therefore characterizes a structure that is complementary or reversed with respect to the structure $\rho(\vec{r})$.

It will be clear that, if we neglect the difference in the absorption coefficients for the structures having electron densities $\rho(\vec{r})$ and $\rho'(\vec{r})$, then the difference between $I(\vec{s})$ and $I'(\vec{s})$ will consist only in the terms corresponding to zero-angle scattering (see the first two terms in Equation 4). If we neglect these terms, which can be done for $s > s_0$, then both intensities are the same, i.e., the scattering intensity is the same for the "direct" structure as for the "reverse" structure (in the sense of Equation 6), and this forms the essence of Babinet's principle. On the basis of the diffraction pattern, therefore, it is impossible to make a choice between the two structures, and for the solution of this question it is necessary to make use of other data.

2. EXPERIMENTAL

In order to solve the problem of "pores or particles" for porous glasses by the use of the low-angle scattering method, the glasses were treated with alkali and with hydrofluoric acid in order to widen the pores artificially. It would be expected that such widening would be accompanied by change in the form of the scattering curve (dependence of intensity on angle), and the direction of this change —to lower or to higher scattering angles— should show whether it is increase in the dimensions of pores or reduction in the thickness of walls that is finding expression.

The first object selected for study was a highly dispersed porous glass prepared from a sodium borosilicate glass containing (in mole-%) 5 of Na_2O, 20 of B_2O_3, and 75 of SiO_2; the low-angle diffraction pattern produced by this glass was sufficiently extensive to permit convenient observation of any changes. A specimen of the original porous glass in the form of a fairly coarse-grained powder (40-70 mesh) was treated with 0.5 N KOH for two hours

(this specimen will be indicated by the symbol KOH-2), washed in running water until the phenolphthalein reaction for alkali was negative, and dried. A second treatment in alkali under the same conditions for a further two hours was then carried out. The same procedure was repeated many times, but in certain cases the duration of the alkaline treatment was limited to one hour. Washing with water after each one- or two-hour treatment with alkali was

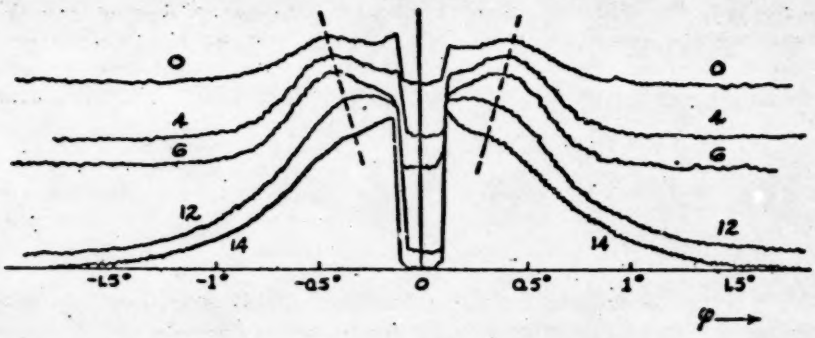

Fig. 2. Microphotometric curves of specimens of highly dispersed porous glass. The numbers indicate the total number of hours for which the glasses were treated with alkali.

carried out in order to effect uniform removal of products of the breakdown of the glass; and washing in running* water prevented the formation of secondary silicic acid by the hydrolysis of silicates and its coagulation in the pores of the glass. We must point out that in the course of this treatment —after the repeated action of alkali (ten hours)— the outward appearance of the powder began to change: whereas at first the flowing water carried away the finest particles of porous glass and the average size of the residual particles was reduced inappreciably by the action of the alkali, after a ten-hour treatment the powder began to change from the granular form into dust; after a fourteen-hour treatment a suspension of the powder in water was like a colloidal solution, and settled extremely slowly.

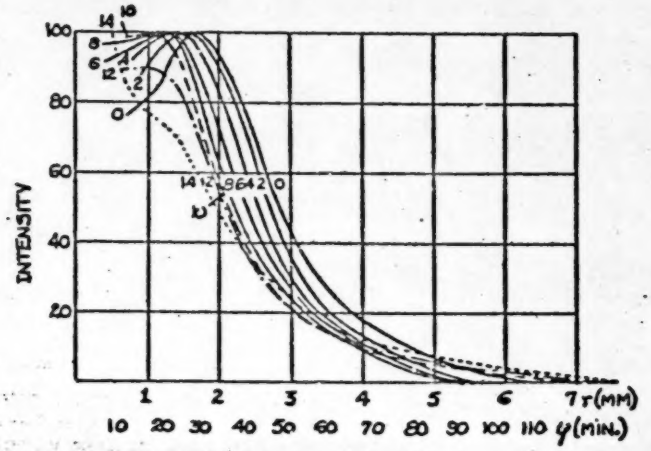

Fig. 3. Intensity curves of highly dispersed porous glass after alkali treatments of varying duration (total number of hours of treatment indicated by numbers).

The X-ray analysis was carried out with CrK_α radiation (λ = 2.29 A), which was rendered monochromatic by reflection at a monocrystal of calcite in the apparatus previously described [3]. Fig. 1 [see plate, page 171] shows two X-ray pictures: one of the original specimen KOH-0, and the other of the specimen KOH-4, i.e., the specimen given two two-hour treatments in alkali. It will be readily seen that scattering due to the first specimen extends at least 1 mm further than that of the second specimen. Microphotometric measurements and the intensity curves derived from the photographic blackening gave convincing confirmation of this result (Figures 2 and 3).

* (Rather than in stationary).

As we were interested above all in the change in the form of the scattering curve as an expression of change in the geometry of the scattering body, we have given the intensity curves of all of the specimens investigated in Fig. 3, in which the height of the interference maximum is taken in each case to be one hundred arbitrary units of intensity. These curves clearly illustrate the regular change in the structure of the porous glass during its treatment with alkali, i.e., during the artificial enlargement of the pores. Since this is accompanied by a regular displacement of the curves toward low scattering angles, we may infer that the dimensions of the regions of inhomogeneity effecting the scattering are increasing, and these may be either particles or pores. But no particles can undergo increase in dimensions as a result of the action of alkali, and we, therefore, reach a conclusion of great importance for the interpretation of the results of low-angle diffraction by porous glasses: the displacement of the scattering curves to smaller angles is a result of increase in pore diameter.*

The regular displacement of the interference maximum to lower scattering angles (Fig. 3) is very marked: its position on the diagram varies from a scattering angle $\varphi = 29.5'$ for the specimen KOH-0 to $\varphi = 19'$ for KOH-10. This displacement evidences the increase in the most frequently realized distance $\underline{d}$ between neighboring scattering centers, i.e., the increase in the sum of the pore and particle diameters (channel width and wall thickness). Increase in channel width, however, must be accompanied by reduced wall thickness, i.e., with maintenance of a constant distance $\underline{d}$ between scattering centers. Hence, this displacement indicates the complete breakdown of some of the thinnest walls with consequent increase of the mean distance $\underline{d}$ (channel + wall).

This interpretation is confirmed by calculations of the radii of the regions of inhomogeneity made after introduction of the collimation correction associated with the use of narrow slits instead of pin-hole diaphragms [7].

Our calculations were based on the relationship

$$I(s) = N\rho^2 v^2 \Phi^2(sR)\left[1 - \frac{\Omega}{V}\Phi(s2R)\right]; \qquad (7)$$

(N is the number of regions of inhomogeneity (particles or pores); $\rho = \rho_a - \rho_b$, in which ρ_a is the average electron density of the particles, and ρ_b is the electron density of the medium filling the spaces between the particles (the pores); $\underline{v}$ is the volume of a single region of inhomogeneity; $\Omega = \frac{4}{3}\pi(2R)^3 N$). Equation 7 can be obtained from Equation 2 (see [4] and [7]), on the assumption that 1) the regions of inhomogeneity have, on the average, the form of identical spheres; 2) their distribution is similar to that of atoms in a compressed gas at equilibrium; and 3) the general picture of scattering from atoms of the gas in their instantaneous configuration is practically indistinguishable (for a sufficiently large number of atoms) from the picture obtained by averaging over all configurations for an arbitrary interval of time.

It may be shown [8] that according to Equation 7 $I(\underline{s})$ shows its principal maximum, on the average, at $sR = 2.0\text{-}2.25$ (its position depends also on $\frac{\Omega}{V}$): This permits us to find, from the position of the maximum, an approximate value of the radius R of particles between which powerful interference effects are being produced. We may note that the condition that $sR = 2.0\text{-}2.25$ can be obtained also from other considerations [9]. On the other hand, since $\Phi(sR)$ falls with angle more slowly than $\Phi(s2R)$ does, at the "greatest" angles (belonging, of course, to the low-angle region) $I(s) \approx N\rho^2 \underline{v}^2 \Phi^2(sR)$, and for the calculation of R we can apply the method of tangents [7, 8] to the "tail" of the curve and assume that $q^2(sR)$ approximates to the corresponding exponents.

Hence, two different methods exist for the calculation of the radius R. However, the results of the determinations of R from the position of the maximum and from the "tail" of the curve may differ greatly from one another in many cases, for in an actual specimen not only particles of identical mean R may exist, but also particles of other dimensions R_i, which, forming, for example, a semblance of a rarified gas ($\Omega \ll V$), will give scattering of the form

$$I(s) = \rho^2 \sum_i N_i v_i^2 \Phi^2(sR_i) \qquad (8)$$

(we assume that $\rho_i = \rho$). This scattering, while only slightly distorting the position of the interference maximum, may greatly affect the scattering picture at the "greatest" angles (i.e., in the region of the "tail" of the curve) in the

* It is of interest to recall an analogous result obtained recently by Guinier [6] for the thermal treatment of an alloy of silver and aluminum. In both cases, the displacement of the maximum to lower angles is interpreted as increase in the radii of regions of inhomogeneity. In correspondence with its dependence on the treatment of the objects investigated, Guinier associated this increase with increase in the size of crystal clusters rich in silver, and we — with increase in pore size. The identical diffraction effect in the two cases is an excellent illustration of the applicability of Babinet's principle to the low-angle scattering of X-rays.

case of low values of R_i, or at the "least" angles in the case of high values of R_i. We may note also that in Equations 7 and 8 Babinet's principle is expressed by the fact that $I(s)$ depends only on the square of the difference $\rho_a - \rho_b$, so that change in the sign of this difference (i.e., transition from the "direct" to the "reverse" structure) has no effect on $I(s)$.

In our calculations, we applied both of these methods. Since the exact determination of the absolute values of pore radii (which depend also on the thermal history of the original glass) was not involved in our problem, our concern being only with their relative changes in the course of alkaline treatments, the collimation correction was made by a highly simplified method [8]. Nevertheless, as can be seen from Table 1, the two methods of calculating the

TABLE 1

Calculation of Pore Radii of Finely Porous Glass

X-Ray Photograph No.	Duration of alkaline treatment (hours)	Pore radius according to position of maximum (A)	Pore radius according to "tail" of curve				
			R_1 (A)	content (% by volume)	R_2 (A)	content (% by volume)	R_{av} (A)
527, 634, 1052	0	64	50	70	107	21	62
1057	2	69	62	75	103	25	72
546, 1033	4	77	65	70	110	30	77
1043	6	85	72	68	115	32	86
547, 1047	8	92	68	62	121	38	88
1035	10	96	47	30	130	70	104
1034	12	100	42	50	100	50	71
1042	14	—	33	70	72	30	45

radii gave agreeing results for all of the specimens, from KOH-0 to KOH-10, and these indicated gradual enlargement of the pores. When the action of the alkali was prolonged (ten hours or more) —as can be seen not only from Table 1, but also from Figures 2 and 3— the variation in the form of the scattering curves takes on a rather different character: extra scattering at the "greatest" angles appears, and the sharpness of the interference maximum is somewhat reduced. This may be explained by incipient destruction of the porous grains of the glass, which results in additional scattering by highly dispersed nonporous particles (radii 47, 42, and 33 A) and in reduction in the intensity of the main scattering by porous grains accompanied by a general increase in the total intensity. This interpretation is confirmed by the increase that occurs in the content by volume of particles of the lowest radii as the action of alkali proceeds, and also by a comparison of the outward appearance of grains of the specimen KOH-6 and KOH-14 under the microscope (magnification 720): whereas in the first case particles of glass of characteristic fracture were clearly visible, in the second case these were replaced by fine formations having uneven edges and rough surfaces. We should point out that the calculation of the second radius for the first five specimens is not completely valid; nor is the calculation of average radii for these samples (Column 8). However, the very close agreement of these values with the values calculated from the position of the maximum justifies this calculation. The calculation of the second radius from the "tails" of curves for specimens treated with alkali for more than ten hours (the last three specimens in Table 1) is of greater validity, since the effect of the interference maximum is here negligible. The fact that this radius is systematically greater than that calculated from the position of the maximum is to be expected: in subtracting the scattering due to particles having the first radius (in this case, nonporous particles) from the general scattering curve, we are bound to include part of the scattering due to the finest pores of intact grains in

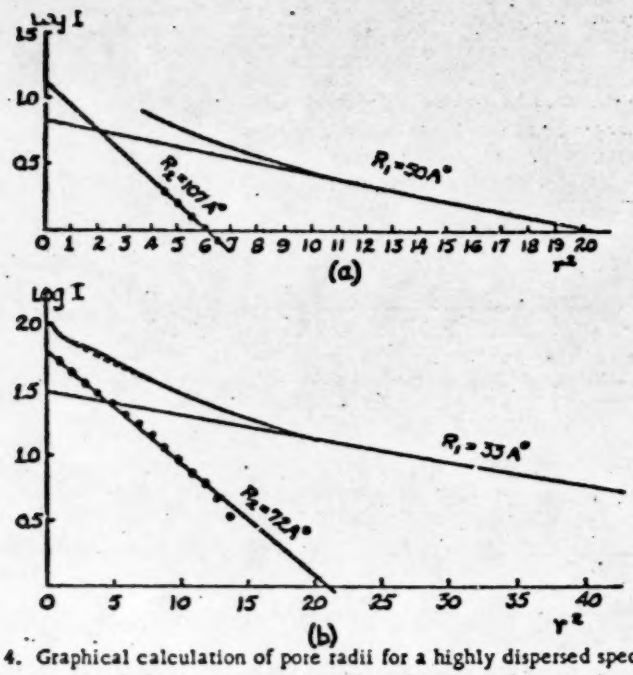

Fig. 4. Graphical calculation of pore radii for a highly dispersed specimen of porous glass: a) before treatment with alkali; b) after a fourteen-hour treatment with alkali.

the subtracted intensity, so that a high value will be obtained for the second radius. In Fig 4 we give two curves illustrating the graphical calculation of the radius from the "tail" of the curve (r is the distance from the center of the primary beam (mm), and is proportional to the scattering angle).

The glass investigated was one of the most highly dispersed, and conclusions arrived at on the basis of its study cannot be extended to more coarsely grained and more coarsely porous specimens without verification. Hence, as a second object for investigation in an analogous way, a specimen having coarser grains and larger pores was taken; it

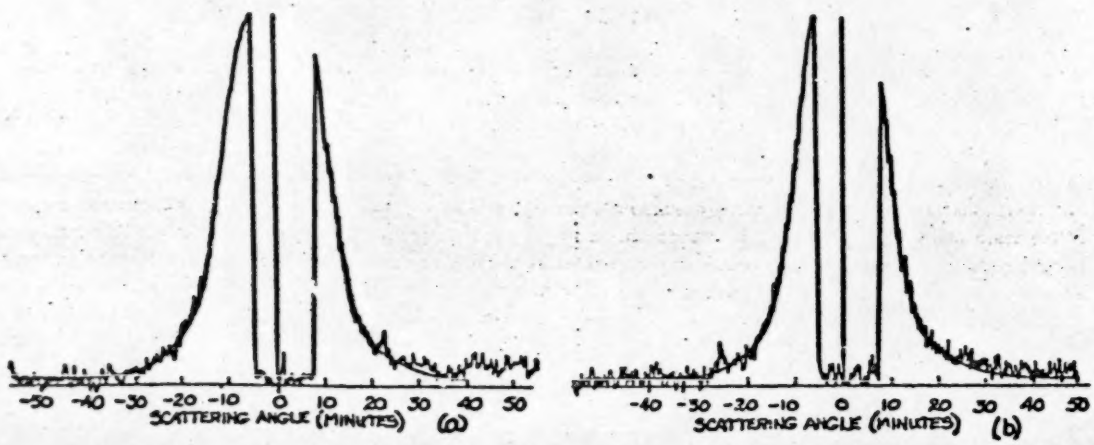

Fig. 5. Microphotometric curves for a coarsely porous glass: a) treated with alkali for eight hours; b) treated further with hydrofluoric acid.

was obtained from a sodium borosilicate glass containing 7% of Na_2O, 23% of B_2O_3, and 70% of SiO_2. Since this sample was much less subject to attack by 0.5 N KOH, it was treated with alkali for eight hours (with washes after every two hours) and with an 8% solution of hydrofluoric acid for 15 minutes. So that the dissolution of the silica skeleton should proceed sufficiently vigorously, not only outside but also inside, the porous glass powder was first placed in a thin-walled glass tube, which was heated to 250-300° and evacuated to a high vacuum; it was then immersed in the hydrofluoric acid and broken, thus ensuring that all of the pores of the specimen were rapidly filled with acid.

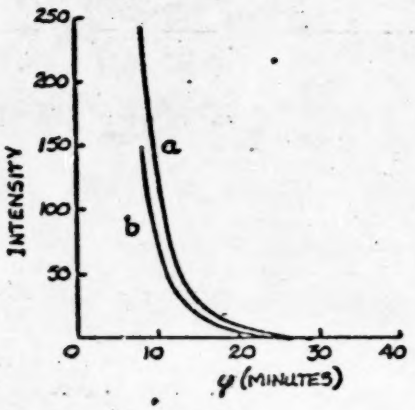

Fig. 6. Intensity curves for coarsely porous glass: a) untreated; b) treated with hydrofluoric acid.

Figures 5 and 6 show the microphotometric and intensity curves for the specimen before and after treatment with hydrofluoric acid (CrK_α radiation; $\lambda = 2.29$ A). They indicate the appreciable enlargement of pores that results from this treatment: the scattering curve for the specimen not treated with hydrofluoric acid (a) falls to zero more slowly than the curve for the treated specimen (b). Calculations made by the method of tangents (Fig. 7) enabled us to obtain three values of "coarse" radii in each case. From the intercepts made by the tangents on the axis of ordinates the relative contents by volume of the pores of each radius were calculated, and the mean radii were also calculated, and were found to be 360 and 400 A, respectively, (Table 2).

The distribution of radii according to size indicates the possible presence of yet larger pores in each sample; the scattering due to these is caught by the trap for the primary beam, the trace of which can be seen in Fig. 1 [see plate, page 171] as a light band in the center (the lowest possible scattering angle was 6.5 minutes of arc). There is no doubt, however, about the increase of the average radius in the region observed; and this confirms the general conclusion of the present investigation, which has removed the difficulty arising in the interpretation of X-ray diagrams owing to the applicability of Babinet's principle to the low-angle scattering of X-rays and has solved the "pores or particles" problem for porous glasses. It was possible to regard the determined values of the radii of the regions of inhomogeneity as the values of the radii of pores, and not of particles, and this result, moreover,

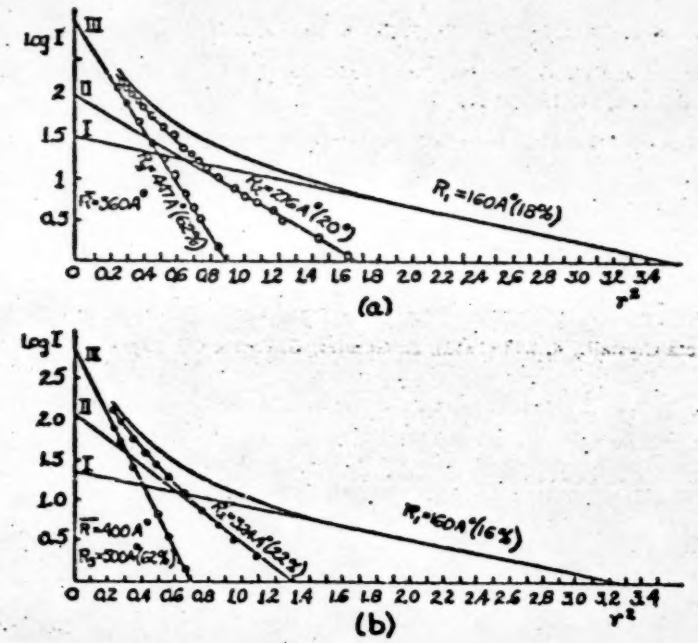

Fig. 7. Graphical calculation of pore radii in a specimen of coarsely porous glass: a) untreated; b) treated with hydrofluoric acid.

was in agreement with investigations on sorption. Only when the destruction of the submicroscopic structure of the specimen was so great that it ceased to be a porous glass —which occurred when it was completely broken down by the prolonged action of alkali— did the diffraction pattern change appreciably owing to the presence of scattering by nonporous particles.

TABLE 2

Calculation of Mean Radii of Dispersed Pores Before and After Treatment with Hydrofluoric Acid

	R_1 (A)	Content (%)	R_2 (A)	Content (%)	R_3 (A)	Content (%)	R_{av} (A)
Before treatment	160	18	276	20	447	62	360
After treatment	160	16	324	22	550	62	400

A further result of this investigation has been a deeper appreciation of the nature of the submicroscopic structure of porous glasses.

SUMMARY

1. The scattering intensities of specimens having the "direct" and "reverse" structures coincide precisely as far as the terms determining the zero-angle scattering: on the basis of the diffraction photograph it is impossible to make a choice between the two structures.

2. By the artificial enlargement of pores in specimens of porous glasses and calculation of the radii of the regions of inhomogeneity that account for the scattering of X-rays at low angles, it has been shown that such a method determines the radii of the pores, and not of the particles.

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Institute of Silicate Chemistry of the
USSR Academy of Sciences

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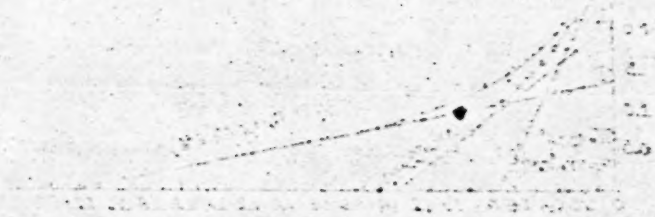

STRUCTURE OF SODIUM BOROSILICATE GLASSES IN ITS RELATION TO THE PHENOMENON OF OPALESCENCE

COMMUNICATION 1. INVESTIGATION OF THE OPALESCENCE OF GLASSES

D. I. Levin, S. P. Zhdanov, and E. A. Porai-Koshits

In spite of the fact that X-ray structural analysis is the most direct method for the determination of the structure of matter in any state of aggregation, practically no X-ray studies of the structure of vitreous materials have been made recently. We consider that this situation has arisen partly owing to an excess of enthusiasm for the application of so-called Fourier Analysis in the interpretation of diffuse and weak diffraction patterns [1]. The absence of other rigorous methods of interpretation and the simplicity of the application of the Fourier method of analysis —in which, with the aid of a single formula and without any obvious a priori assumptions concerning the structure of the material, the experimental intensity curve is transformed unequivocally into the curve for the radial distribution of atoms— have made this method extremely attractive. However, the averaging introduced in this mathematical treatment of diffraction patterns leads to the complete leveling of the fine structural details, and the resulting curves for the distribution of atoms cannot make any appreciable contribution to the theory of the vitreous state.

We consider that it is more useful to combine purely X-ray methods with other methods capable of giving valuable information concerning the structure of complex glasses. In this connection the selection of the object for investigation is of great importance. For this purpose we have selected alkali borosilicate glasses, which are very suitable owing to the considerable changes that occur in a number of their properties when small changes are made in their composition and thermal treatment; this applies particularly to their property of exhibiting opalescence in varying degree. Also, we have made use of their peculiar property of being susceptible to leaching with formation of so-called porous glasses, the properties of which are closely related to those of the original glasses. By a study of the opalescence of the latter and comparison of the results with those on the structure of the porous glasses, investigated by several independent methods, it is possible greatly to supplement the conclusions derived from a study based purely on X-ray examination.

In this paper, after an examination of present-day views on the causes of opalescence in sodium borosilicate glasses, we describe the results of the experimental study of opalescence. In a future communication we shall give the results of investigations into the structure of the porous products of the leaching of these glasses. Three independent methods of investigation (sorption, X-ray scattering at low angles, and electron microscope studies) are used.

In a third communication we shall make a comparison of the results of the investigations on the original and on the porous glasses and make an attempt to describe the structure of sodium borosilicate glasses on the basis of the experimental material obtained.

Survey of Existing Views on the Causes of Opalescence in Sodium Borosilicate Glasses

At the present time there is no single unified point of view with regard to the causes of the opalescence that occurs in certain glasses. The question of the causes of opalescence in sodium borosilicate glasses is even more obscure. According to patent specifications relating to the glass "Vycor" [2] and to a paper by one of the authors of these specifications [3], the opalescence of sodium borosilicate glasses is the result of their separation into two phases, one of which is siliceous, and the other is enriched in sodium oxide and boric anhydride. This separation of sodium borosilicate glasses of certain compositions into two phases occurs when they are maintained within a definite temperature range. Both phases are regarded as vitreous, since the investigation of opalescent sodium borosilicate glasses by means of the microscope or X-rays has not resulted in the detection of any crystalline formations. A similar view on the causes of opalescence in sodium borosilicate glasses has been expressed by Sotvinkin [4], who maintains that, as a result of segregation during slow cooling, a colloidal solution of glass in glass is formed, and that it is possible in certain cases to observe, with the aid of the ultramicroscope, the presence of extremely fine particles of dispersed phase in glass that has undergone this segregation process.

Porai-Koshits [5] has investigated the scattering of X-rays by a sodium borosilicate glass of composition

Na 70-23.* By an analysis of the X-ray pattern, Porai-Koshits showed that there was an increase in the degree of order of the sodium borate component when the glass was held at the temperature of the opalescence zone. As is well-known, such thermal treatment results in an increase in the degree of opalescence. On this basis the author concluded that the opalescence of sodium borosilicate glasses results from the growth of borate crystallites. The disappearance of opalescence with further rise in temperature was explained as being due to the melting of these crystallites. It must be remembered, however, that, even when the glass is kept for a long time in the temperature range of the opalescence zone, the X-ray results indicate only slight amount of growth in the crystallites (not more than a few angstroms), whereas the intensity of the opalescence increases in this treatment by hundreds and thousands of times (see the next section). It appears doubtful whether such a small increase in the dimensions of the crystallites could be the cause of the extremely high observed increase in the intensity of opalescence.

Grebenshchikov and Molchanova [6], who made a detailed study of sodium borosilicate glasses, did not make any definite assertion regarding the causes of the opalescence of these glasses; they state, however, that "at temperatures corresponding to the appearance of opalescence, there is an increase in the size of the amicroscopic sodium borate crystallites, which form still larger, though still submicroscopic, crystals, which are directly in contact with one another". It would appear to follow from this quotation that the authors associate the appearance of opalescence with growth of sodium borate crystallites, i.e., that they hold the view expressed by Porai-Koshits in one of his earlier papers as discussed above.

Weyl, in a short review of the method of preparation of the glass "Vycor" and its properties [7], associates the opalescence of sodium borosilicate glasses with the separation of a previously homogeneous glass into two phases having different optical properties. According to Weyl, one of the phases is almost pure silica, and the other consists of alkali borates in a vitreous or finely crystalline form.

Sodium borosilicate glasses that do not show opalescence are regarded as homogeneous. This view, however, is contrary to the fact that porous glasses can be prepared from clear sodium borosilicate glasses that do not exhibit visible opalescence. It is evident that separation into two "phases" occurs also in the case of non-opalescent glasses. It has been shown by one of the authors of this paper [8, 9] that the difference in structure between opalescent and non-opalescent sodium borosilicate glasses cannot be regarded as fundamental, but is only a question of difference in degree of heterogeneity. Molchanova and coworkers [10, 11] consider that the opalescence of sodium borosilicate glasses is associated with the separation from the glass of some dispersed phase in such insignificant amount that this separation cannot affect the chemical properties of the glass.

An original view on the causes of the opalescence of sodium borosilicate glasses has recently been advanced by Abe [12]. In the opinion of this author, opalescence can occur in sodium borosilicate glasses only when the main constituents of the glass are supplemented by small amounts of modifying oxides having a cation valency of three or more, for example V_2O_5, MnO_2, As_2O_5, and Fe_2O_3. An addition of about 1% of such oxides is sufficient to cause opalescence. The temperature for maximum opalescence does not depend on the basic composition of the glass, but depends on the nature of the added modifying oxide. The author states that X-ray investigation of the opalescent glass provides a basis for the view that "ultramicroscopic crystals of cristobalite" are present. According to this investigator, opalescence does not result directly from the separation of sodium borosilicate glasses into two phases. Such a separation, however, appears to be a necessary prerequisite for the development of opalescence. The author considers that the direct cause of opalescence is the crystallization of cristobalite in the form of ultramicroscopic crystals, which can occur in a phase rich in SiO_2. The crystallization of cristobalite becomes possible only after the separation of the glass into two phases; such separation, therefore, must always precede opalescence. The ability of sodium borosilicate glasses to separation into two phases is to be explained by the tendency in such glasses to the formation of groupings consisting of one $[BO_4]$ tetrahedron surrounded by four $[BO_3]$ triangles.

Objections can be raised to these ideas of Abe concerning opalescence. It cannot be considered that the statement that opalescence occurs only when the main constituents of alkali borosilicate glasses are supplemented by additions of oxides having a cation valency of three or more is sufficiently well-grounded. It is known that oxides of tervalent metals encourage the transition of sodium borosilicate glasses into the opalescent state and that the addition of such oxides as MgO and CaO also greatly increases their opalescence. It is known also that sodium borosilicate glasses that contain no additives also show opalescence [6, 8, 2].

Also, it is impossible to agree with the author's assertion that the temperature for maximum opalescence does not depend on the basic composition of the glass. This is contradicted by data that we have at our disposal, and also by published data [6].

* Of the figures denoting the composition, the first is the silica content (mole-%), the second is the boron anhydride content (mole-%); the remainder consists of sodium oxide.

As regards the explanation of opalescence by the formation of ultramicroscopic crystals of cristobalite, this also cannot be regarded as satisfactory, since it is contrary to common sense and to experimental facts. In actual fact, the zone for the opalescence of the majority of sodium borosilicate glasses can be regarded as the temperature range 550-700° (see the next section). The crystallization of silica, however, generally begins at higher temperatures, so that between the two zones there is a zone of completely transparent glass. If the cause of opalescence were the crystallization of silica, it would be quite incomprehensible why the submicroscopic crystals of cristobalite formed should suddenly disappear when the temperature was raised and then appear again at a higher temperature. Only by prolonged maintenance of the glass at a temperature of about 700° can the two zones (opalescence and devitrification) be made to overlap, and they are easily distinguished visually: crystallization extends inward from a rough surface, whereas the opalescence of the glass occurs uniformly through the whole volume and the surface preserves its smoothness. Also, a more careful X-ray investigation by one of the authors of this paper [13] has shown that, when sodium borosilicate glasses are subjected to prolonged heating, sodium borates may crystallize out, but in no case was crystallization of silica detected within the opalescence zone.

It will be seen, therefore, that the causes of the opalescence of sodium borosilicate glasses still remain obscure. It must be pointed out that no quantitative study of the scattering of light by sodium borosilicate glasses has yet been carried out.

EXPERIMENTAL

Investigation of the Opalescence of Sodium Borosilicate Glasses

Rayleigh scattering in certain sodium borosilicate glasses is peculiar in that, under definite conditions of thermal treatment (keeping of the glass in the temperature range 550-700°), it increases until an opalescent state is attained. The intensity of the opalescence may vary within wide limits: from opalescence that is invisible to the unaided eye to such strong opalescence that the glass becomes opaque. The phenomenon of opalescence occurs in sodium borosilicate glasses having certain compositions. There can be no doubt that it is associated with peculiarities in the structures of these glasses and can be utilized not only in the study of their structures, but also in the elucidation of the question of the nature of Rayleigh scattering in glasses in general.

The procedure used in the study of the variation in the scattering by sodium borosilicate glasses when subjected to thermal treatment has been described previously [14]; it was as follows. The variation in the intensity and depolarization of the light scattered at 90° was studied by visual photometry. The intensity was measured with a star photometer, and depolarization was measured by Cornu's method with the aid of a Wollaston prism and a nicol. The sample under investigation was placed in a furnace provided with windows for the entry of the incident and exit of the scattered light. The intensity and depolarization measurements could be made without adjustment of the sample in the furnace. The light source was a SVD mercury lamp. In order to exclude fluorescence, a ZhS-8 glass filter, which cuts out the short-wave part of the spectrum up to 5000 A, was interposed in the incident beam. As a standard of scattering intensity, a sample of optical glass was used, and the intensity of the scattering produced by this was compared with the intensity of the molecular scattering of diethyl ether. Glasses of four different compositions were investigated: Na 70-23, Na 65-30, Na 60-37, and Na 60-30.

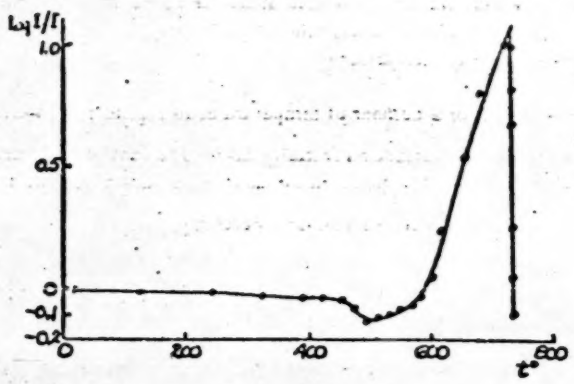

Fig. 1. Dependence of the intensity of the scattered light on temperature for the glass Na 70-23.

Fig. 1 shows the curve for the variation of scattering intensity with temperature for the glass Na 70-23, and this is typical for all of these glasses. The value of $\log \frac{I}{I_0}$ is plotted along the ordinate axis (I is the scattering intensity at a given temperature; I_0 is the scattering intensity at 20°. Measurements were made after the glass had been maintained at the given temperature for ten minutes. It will be seen from Fig. 1 that, according to the nature of the variation in the scattering, the following temperature ranges can be distinguished:

1. The low temperature range (room temperature to 550°), in which the scattering intensity diminishes with rise in temperature.

2. The range extending approximately from 550° to 700°, in which the scattering intensity rises steeply, i.e., the opalescence range.

3. The range in which opalescence disappears (above 700°): the scattering intensity falls to the values observed for optical glasses.*

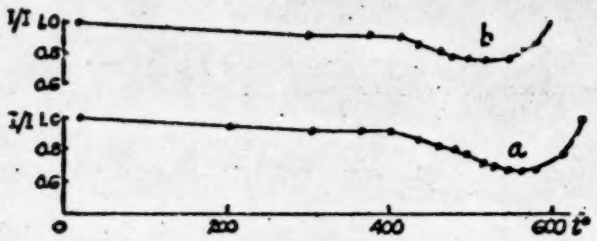

Fig. 2. Variation of the scattering intensity in the first temperature range for opalescent and non-opalescent samples of the glass Na 65-30:
a) $\frac{I_0}{I_{ether}} = 1000$; b) $\frac{I_0}{I_{ether}} = 6$.

At low temperatures the course of the curve for the variation in scattering intensity depends very little on the absolute value of the intensity. This can be clearly seen from Fig. 2, in which a comparison is made of such curves for opalescent and non-opalescent samples of the glass Na 65-30 (curves a and b, respectively). From Fig. 2 it will be seen also that for the opalescent glass the minimum of I/I_0 is more marked than that of the non-opalescent glass, and its position is displaced in the direction of higher temperatures. These phenomena evidently depend on the thermal history of the glass.

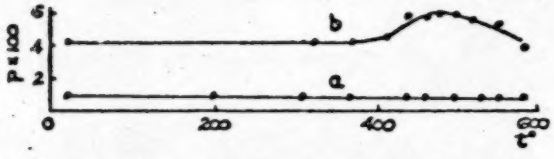

Fig. 3. Dependence of depolarization on temperature for opalescent and non-opalescent samples of the glass Na 65-30: a) $\frac{I_0}{I_{ether}} = 1000$; b) $\frac{I_0}{I_{ether}} = 6$.

It was further found that for non-opalescent glasses a rise in the depolarization ρ occurs in the region of the minimum value of I/I_0. For strongly opalescent glasses, for which the values of ρ are low (not greater than 0.01), no variation of ρ is observed. Fig. 3 shows the variation of the depolarization ρ with temperature for the same samples of glass Na 65-30. The rise in ρ with simultaneous fall in I/I_0 indicates that it is not the whole of the scattered light that is changing in intensity, but mainly its polarized component.

In the low-temperature range the variation in the scattering is almost reversible with respect to temperature. In the opalescence range the variation in the scattering is irreversible. The intensity of the scattering depends both on the temperature and on the time for which the sample is held at that temperature. The character of the dependence is shown by the curves in Fig. 4 for the glass Na 70-23, and it will be seen that the higher the temperature, the higher the rate at which the scattering intensity increases.**

The depolarization as a function of $\log \frac{I}{I_{ether}}$ is shown for a number of temperatures in Fig. 5, from which it will be seen that with increase in the scattering intensity the depolarization initially falls. The scattering increases, therefore, mainly at the expense of the polarized component. The sharp rise in the depolarization, beginning from $\log \frac{I}{I_{ether}} \approx 2.6$, is evidently associated with the appearance of a strong secondary scattering.

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* The scattering intensity of the glass that had become transparent was determined after quenching from temperatures above the opalescence region and repolishing to remove the crystallized layer.

** For temperatures up to 638° the scattering intensity does not attain any definite limit. The limit $\log \frac{I}{I_{ether}} \approx 3.8$, to which the scattering intensity tends at temperatures of 663° and higher, is an apparent limit. This limit is associated with the reduction in the intensity of the incident beam in its passage through a strongly scattering sample [14]. In our case, for a 15-mm length of sample, the effect of the reduction in the intensity of the incident beam on the measurements became apparent at values of $\log \frac{I}{I_{ether}} > 2.5$.

At temperatures at which opalescence disappears, quantitative measurements become difficult: owing to their low viscosity the samples begin to flow and crystallization of SiO_2 sets in at the surface. Nevertheless, by a study of the direction of the change in scattering intensity it is possible to estimate a temperature range below which opalescence appears and above which it disappears. Fig. 6 shows the directions of the changes in scattering intensity for

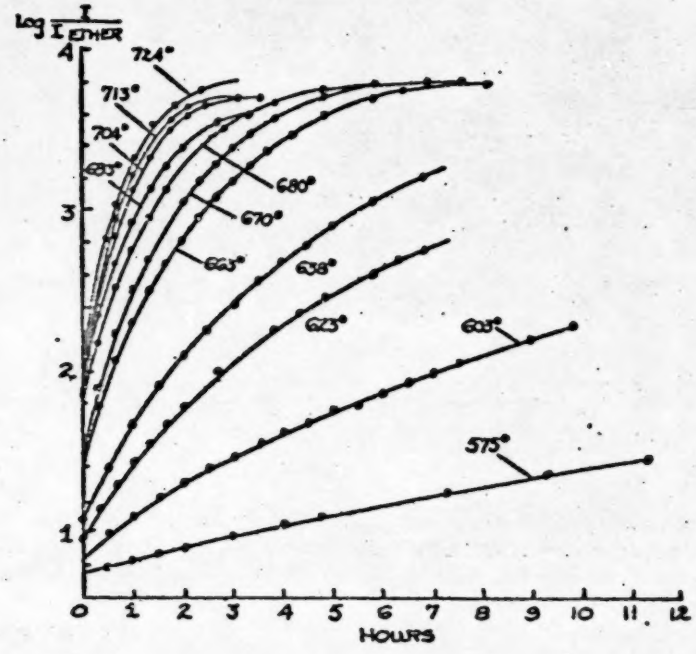

Fig. 4. Dependence of the scattering intensity on the time for which the glass Na 70-23 is held at different temperatures.

the same sample Na 70-23, which was held successively at a number of closely spaced temperatures. It will be seen from Fig. 6 that the range sought comprises not more than 2-3°, so that in a certain sense we may speak of a critical temperature for the disappearance of opalescence. It was found that the value of the critical temperature may vary, not only for glasses of different compositions, but also for glasses of the same composition, but from different meltings.

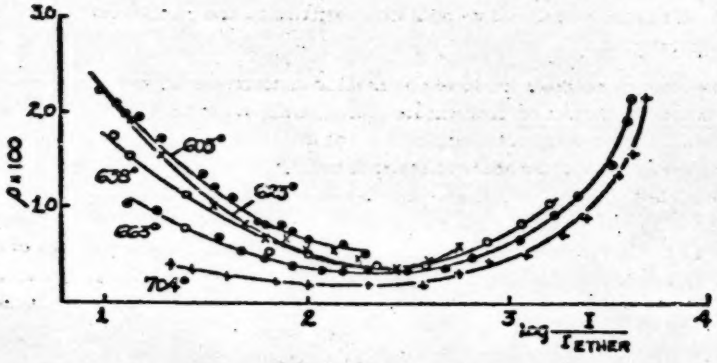

Fig. 5. Dependence of the depolarization on the scattering intensity for the glass Na 70-23.

In sodium borosilicate glasses that do not show opalescence, for example Na 60-20, and in optical (flint) glasses, the phenomena described here, in particular the fall in scattering intensity with temperature in the range 20-550°, are not found. This constitutes evidence for the presence of structural peculiarities in glasses capable of developing opalescence. Examination of the compositions of such glasses shows that they belong to the group of

ternary glasses that are able to form porous products when subjected to leaching by acid solutions [6, 4, 3]. The field of the compositions of these glasses, however, does not coincide with any definite phase field of the ternary melting-point diagram, but covers only a part of the silica field. The crystallizing tendency of sodium borosilicate glasses is also not associated in any way with the boundaries of this field, and the phenomena described here, in particular the sharp rise in opalescence at temperatures from 550° to 700°, cannot be explained by incipient crystallization processes.

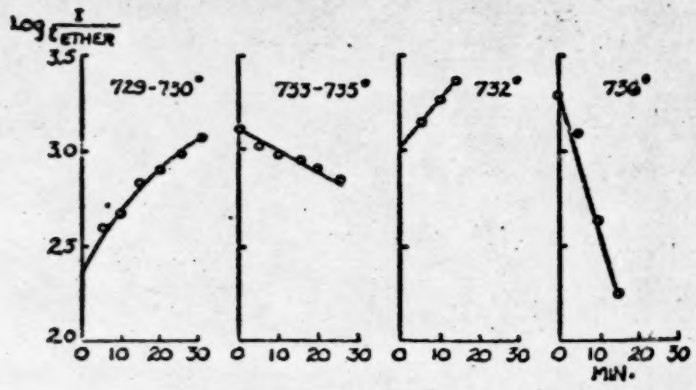

Fig. 6. Determination of the temperature of the disappearance of opalescence.

The boundaries of the field of opalescent (and leachable) glasses cannot be associated with any effects in the smooth variation with composition of density, refractive index, coefficient of thermal expansion, and so on, at temperatures below 1000° (see, for example, [12]), and also with the position and magnitude of the diffuse endothermic effect observed for all sodium borosilicate glasses in the temperature range 400-600°. Attempts to establish the presence of chemical compounds in sodium borosilicate glasses by the method of thermal analysis have not yielded positive results [13].

The results of the investigation described above show, above all, the unsatisfactory nature of the accepted explanations of Rayleigh scattering in glasses as caused by "frozen-in" density fluctuations, deformations, or fortuitous optical heterogeneities. These results have established an undoubted relationship between the intensity of Rayleigh scattering and the structure of the investigated glasses. The latter, in its turn, has been found to be dependent not only on the composition of the glasses, but also on their thermal treatment, or on the previous thermal history of the samples. At the same time we have succeeded in establishing certain quite general regularities characteristic of all of the compositions investigated (for example, the existence of three temperature zones for the changes in the scattering intensity, the reversibility of these changes in the first zone, their nonreversibility in the opalescence zone, and so on), and on the basis of these it should be possible to arrive at some more definite conclusions regarding the structure of the glasses investigated.

Even these investigations, however, have not enabled us to give a definite answer to the fundamental question of the causes of opalescence in sodium borosilicate glasses; still less can they explain the anomalous temperature variation of the intensity of Rayleigh scattering in each of the above-mentioned temperature zones. For the answer to this question it is necessary that our study of the structure of opalescent sodium borosilicate glasses should go deeper than it is possible to go by the simple comparison of their various properties. It appeared to us that a promising line of approach is provided by the undoubted relationship between the ability of such glasses to become opalescent and their ability to form porous glasses by leaching, as discussed above; the results of the study of the structure of the latter could be applied to the solution of the question of the nature of opalescence, and also to the elucidation of the essential nature of processes occurring during the thermal treatment of the original glasses.

SUMMARY

1. Existing views on the causes of opalescence in sodium borosilicate glasses are mutually contradictory and are not based on the quantitative study of the scattering of light in these glasses.

2. Investigation of Rayleigh scattering in sodium borosilicate glasses has established beyond doubt that there is a relationship between the scattering intensity and the structure of the glass. It has been shown that there are three temperature zones characterized by the way in which the intensity varies: a zone in which the intensity falls with rise in temperature, the opalescence zone, and the zone in which opalescence disappears.

3. In order to interpret the observed regularities, a deeper study of the structure of sodium borosilicate glasses will be necessary. A promising line of approach can be based on the relationship between the ability of sodium borosilicate glasses to become opalescent and their ability to form porous glasses by leaching, the structure of the latter being open to investigation by several independent methods.

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Institute of Silicate Chemistry of the
USSR Academy of Sciences

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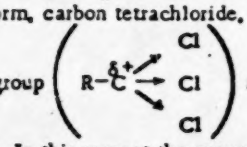
PREPARATION OF CARBOXYLIC ACIDS OF STRUCTURE $CCl_3(CH_2)_nCOOH$ AND $CCl_2{=}CH(CH_2)_nCOOH$, AND THEIR DISSOCIATION CONSTANTS

A. N. Nesmeyanov, L. I. Zakharkin and R. Kh. Freidlina

Compounds containing the trichloromethyl group have now become readily accessible by the addition reactions given by chloroform, carbon tetrachloride, and bromotrichloromethane with olefins. According to its structure, the trichloromethyl group  must be classified with electron-acceptor substituents (orienting groups of the second kind). In this respect the group is of particular interest, since it does not contain double bonds and so cannot be in π,π-conjugation with double bonds or with the benzene ring. The investigation of the orienting effect of the trichloromethyl group for electrophilic substitution in the aromatic nucleus has yielded contradictory results. Thus, the trichloromethyl group of benzotrichloride orients meta in nitration and ortho-para in chlorination [1].

At attempt to determine the orienting effect of the trichloromethyl group on the electrophilic addition of hydrogen bromide to 3,3,3-trichloropropene showed that in absence of catalysts no reaction occurred, while in presence of $AlCl_3$ the 3,3,3-trichloropropene isomerized into 1,1,3-trichloropropene [2]. It has also not been found possible to detect any tendency of the trichloromethyl group in saturated polychloro hydrocarbons to enter into reaction with nucleophilic reagents, probably owing to the screening of the center of nucleophilic attack by the three chlorine atoms [3]. Up to the present, therefore, there are no direct experimental data on which to base the classification of the trichloromethyl group as an electron-accepting substituent. It is thus of interest to study the effect of the trichloromethyl group on other functional groups. Herein, we describe the synthesis of a number of carboxylic acids $CCl_3(CH_2)_nCOOH$ and $CCl_2{=}CH{-}(CH_2)_nCOOH$, and we give their dissociation constants, which have been determined in order to show the effect of the CCl_3 and $CCl_2{=}CH$ groups on the carboxyl group for varying lengths of intervening chain. The only previously known members of the series of CCl_3-containing carboxylic acids are trichloroacetic, 4,4,4-trichlorobutyric [4], and 7,7,7-trichloroheptanoic [5] acids. Attempts to prepare 3,3,3-trichloropropionic acid by the hydrolysis of its ethyl ester were not successful [6]. Of the carboxylic acids containing the $CCl_2{=}CH$ group, 3,3-dichloroacrylic and 4,4-dichloro-3-butenoic [7] acids have been described. We have synthesized the acids $CCl_3(CH_2)_nCOOH$ (n = 2-6) and $CCl_2{=}CH{-}(CH_2)_nCOOH$ (n = 1-6).

5,5,5-Trichlorovaleric acid was prepared according to the scheme:

$$CCl_3(CH_2)_4Cl \rightarrow CCl_3(CH_2)_4OCOCH_3 \rightarrow CCl_3(CH_2)_4OH \rightarrow CCl_3(CH_2)_3COOH.$$

Oxidation of the trichloropentanol was effected with chromic anhydride in glacial acetic acid, when, in addition to 5,5,5-trichlorovaleric acid, 5,5,5-trichlorovaleraldehyde and the 5,5,5-trichlorcpentyl ester of 5,5,5-trichlorovaleric acid were formed. 6,6,6-Trichlorohexanoic acid and 8,8,8-trichlorooctanoic acid were prepared in accordance with the scheme:

$$CCl_3(CH_2)_nCl \rightarrow CCl_3(CH_2)_nCN \rightarrow CCl_3(CH_2)_nCOOH,$$

(n = 4 and 6).

When 8,8,8-trichlorooctanenitrile was hydrolyzed with concentrated sulfuric acid, suberic acid was obtained in almost quantitative yield. 5,5-Dichloro-4-pentenoic, 7,7-dichloro-6-heptenoic, and 9,9-dichloro-8-nonenoic acids were prepared according to the scheme:

$$CCl_2{=}CH(CH_2)_nCl + CH_2(COOC_2H_5)_2 \xrightarrow{C_2H_5ONa} CCl_2{=}CH{-}(CH_2)_nCH(COOC_2H_5)_2 \rightarrow CCl_2{=}CH{-}(CH_2)_{n+1}COOH,$$

(n = 1, 3 and 5).

An attempt to prepare 5,5-dichloro-4-pentenoic acid by the oxidation of 5,5-dichloro-4-penten-1-ol did not give the desired result owing to the action of the oxidizing agent on the $CCl_2{=}CH$ group. 6,6-Dichloro-5-hexenoic and 8,8-dichloro-7-octenoic acids were prepared according to the scheme:

$$CCl_2{=}CH{-}(CH_2)_nCl \rightarrow CCl_2{=}CH{-}(CH_2)_n\,CN \rightarrow CCl_2{=}CH{-}(CH_2)_nCOOH,$$

(n = 3 and 5).

All of the CCl_3-containing acids obtained are low-melting crystalline substances; the acids containing the CCl_2=CH group are liquids. Owing to the insolubility of the higher members of the series in water, the dissociation constants were determined in a 50% by weight methanol solution for all of the acids, and also in water for the first two members of each series. The results obtained are given in Tables 1 and 2.

TABLE 1

Dissociation Constants in a 50% by Weight Methanol Solution at 25°

n	2	3	4	5	6	7
$CCl_3(CH_2)_nCOOH$	$4.6 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$	$1.25 \cdot 10^{-6}$	$9.55 \cdot 10^{-7}$	$8.95 \cdot 10^{-7}$	
$CCl_2=CH-(CH_2)_{n-1}COOH$	$5.95 \cdot 10^{-6}$	$1.45 \cdot 10^{-6}$	$9.25 \cdot 10^{-7}$	$8.75 \cdot 10^{-7}$	$7.75 \cdot 10^{-7}$	$6.3 \cdot 10^{-7}$

TABLE 2

Dissociation Constants in Water at 20°

$CCl_3CH_2CH_2COOH$	$6.2 \pm 0.1 \cdot 10^{-5}$	$CCl_2=CH-CH_2-COOH$	$9.1 \pm 0.1 \cdot 10^{-5}$
$CCl_3CH_2CH_2CH_2COOH$	$3.0 \pm 0.1 \cdot 10^{-5}$	$CCl_2=CH-CH_2-CH_2-COOH$	$2.7 \pm 0.1 \cdot 10^{-5}$

For comparison we may cite the dissociation constants of butyric and valeric acids at 18°, which are $1.53 \cdot 10^{-5}$ and $1.51 \cdot 10^{-5}$, respectively [8]; of 4-chlorobutyric and 5-chlorovaleric acids at 25°, which are $3 \cdot 10^{-5}$ and $2.04 \cdot 10^{-5}$, respectively [9]; and of 4,4,4-trifluorobutyric and 5,5,5-trifluorovaleric acids at 25°, which are $6.98 \cdot 10^{-5}$ and $3.2 \cdot 10^{-5}$, respectively [10; 11]. The inductive effect of the CCl_3 group results in a quite definite increase in the acidity, as compared with the unsubstituted acids, even in 5,5,5-trichlorovaleric acid, in which the CCl_3 and COOH groups are separated by three methylene groups. Increase in the number of chlorine atoms from one to three also results in an appreciable increase in the dissociation constant in the case of butyric and valeric acids. The difference in the effects of the trifluoro- and trichloro-methyl groups falls with increase in the number of methylene groups, and it becomes inappreciable already for valeric acid. The dissociation constants change greatly as we pass from the C_4 to the C_5 acids, and then change very little. It is interesting to note that 4,4-dichloro-3-butenoic acid has a higher dissociation constant than 4,4,4-trichlorobutyric acid, i.e., two chlorine atoms in the first acid have a greater effect than three chlorine atoms in the second; but in the succeeding acids the relationship is reversed. This behavior is probably to be associated with the fact that in 4,4-dichloro-3-butenoic acid the CCl_2=CH and COOH groups are separated by only one CH_2 group. For the acids studied, no feature can be discerned in the mode of variation of the dissociation constants that can be associated with the oddness or evenness of the number of methylene groups separating the two functional groups.

EXPERIMENTAL

The dissociation constants were calculated from the pH values of partly neutralized solutions of the acids; the activity coefficient was taken as unity. The pH measurements were carried out on an LP-4 potentiometer with glass and calomel electrodes. The acids containing a dichlorovinyl group were vacuum-distilled in a current of nitrogen before the determinations.

4,4,4-Trichlorobutyric acid was prepared by hydrolysis of the corresponding nitrile [4] with a mixture of acetic and hydrochloric acids; b.p. 102-103° (2.5 mm); m.p. 55°; the literature [4] gives m.p. 55°. The anilide of 4,4,4-trichlorobutyric acid has m.p. 159-160° (from benzene-ligroin).

	Found %	N 5.11 5.19
$C_{10}H_{10}Cl_3NO$.	Calculated %	N 5.25

5,5,5-Trichloro-1-pentanol acetic ester. A solution of 42 g of 1,1,1,5-tetrachloropentane, 25 g of potassium acetate, and 1 g of potassium iodide in 80 ml of glacial acetic acid was heated under reflux for 18 hours. The mixture was cooled, water was added, and the oil that separated was extracted with chloroform. The chloroform solution was washed with sodium carbonate solution and dried with sodium sulfate. The solvent was removed, and the residue was vacuum-distilled, when it yielded 37.4 g (80%) of the acetic ester of 5,5,5-trichloro-1-pentanol, b.p. 99-100° (3.5 mm); n_D^{20} 1.4700; d_4^{20} 1.2859; found MR 50.66; calculated MR 50.78.

	Found %	C 35.62; 35.77; H 4.93; 4.91
$C_7H_{11}Cl_3O_2$.	Calculated %	C 35.97; H 4.71

5,5,5-Trichloro-1-pentanol. A solution of 70.5 g of 5,5,5-trichloro-1-pentanol acetic ester in 60 ml of methanol containing 1 ml of concentrated hydrochloric acid was set aside for 24 hours. The excess of methanol and methyl acetate was then distilled off from a water bath. The residue was again dissolved in 60 ml of methanol containing 1 ml of concentrated hydrochloric acid, and the solution was heated under reflux for three hours. The methanol was removed, and the residue was vacuum-distilled, when it yielded 57 g (99%) of 5,5,5-trichloropentanol, b.p. 112-112° (10 mm); n_D^{20} 1.4897; d_4^{20} 1.3431; found MR 41.20; calculated MR 41.41.

	Found %:	C 31.07; 31.31; H 4.84; 4.90
$C_5H_9Cl_3O$.	Calculated %:	C 31.38; H 4.70

5,5,5-Trichlorovaleric acid. Chromic anhydride (7 g) was added slowly to a stirred cooled solution of 19 g of 5,5,5-trichloro-1-pentanol in 50 ml of glacial acetic acid, and the mixture was set aside for four hours at room temperature. Water was then added, and the oil that separated was extracted with chloroform. The chloroform extract was washed with sodium carbonate solution and dried with sodium sulfate. When the alkaline solution was acidified, 5,5,5-trichlorovaleric acid was precipitated and was collected on the filter and washed with water. A yield of 4.5 g of acid, m.p. 65-66° (from petroleum ether) was obtained.

	Found %:	C 29.36; 29.27; H 3.48; 3.65
$C_5H_7Cl_3O_2$.	Calculated %:	C 29.19; H 3.40

The anilide of 5,5,5-trichlorovaleric acid has m.p. 117-118° (from benzene-ligroin).

	Found %:	N 4.99; 4.85
$C_{11}H_{12}Cl_3NO$.	Calculated %:	N 4.99

Two fractions were separated when the chloroform solution was vacuum-distilled: Fraction I, b.p. 103-104° (8 mm), 3.2 g; and Fraction II, b.p. 164-165° (1.5 mm), 7.1 g. Fraction I was 5,5,5-trichlorovaleraldehyde, n_D^{20} 1.4890; d_4^{20} 1.3662; found MR 40.06, calculated MR 39.91.

	Found %:	C 31.51; 31.50; H 3.91; 3.85
$C_5H_7Cl_3O$.	Calculated %:	C 31.66; H 3.70

Its dinitrophenylhydrazone melted at 133-134°.

	Found %:	Cl 28.80; 28.77
$C_{11}H_{11}Cl_3N_4O_4$.	Calculated %:	Cl 28.82

Fraction II was the 5,5,5-trichloropentyl ester of 5,5,5-trichlorovaleric acid, n_D^{20} 1.500; d_4^{20} 1.4060; found MR 79.34; calculated MR 79.24.

	Found %:	C 44.19; 44.21; H 5.01; 5.20
$C_{10}H_{14}Cl_6O_2$.	Calculated %:	C 44.03; H 5.13

6,6,6-Trichlorohexanoic acid. A solution of 20 g of 6,6,6-trichlorohexanenitrile in a mixture of acetic and hydrochloric acids (80 ml of glacial acetic acid, 30 ml of concentrated hydrochloric acid, and 20 ml of water) was heated under reflux for eight hours. Part of the acetic acid was then driven off under reduced pressure, water was added to the residue, and the oil that separated was extracted with chloroform. The product was 18.1 g (82%) of 6,6,6-trichlorohexanoic acid, b.p. 114-115° (1 mm); m.p. 50-51° (from petroleum ether).

	Found %:	C 33.03; 32.90; H 4.04; 4.08
$C_6H_9Cl_3O_2$.	Calculated %:	C 32.80; H 4.10

The anilide of 6,6,6-trichlorohexanoic acid melts at 109-110°

	Found %:	N 4.96; 4.84
$C_{12}H_{14}Cl_3NO$.	Calculated %:	N 4.75

7,7,7-Trichloroheptanoic acid was prepared as previously described [5].

The anilide of 7,7,7-trichloroheptanoic acid melts at 98-99°.

	Found %:	N 4.58; 4.58
$C_{13}H_{15}Cl_3NO$.	Calculated %:	N 4.54

8,8,8-Trichlorooctanenitrile. A mixture of 90 g of 1,1,1,7-tetrachloroheptane, 30 g of sodium cyanide in 60 ml of water, and 250 ml of alcohol was heated with stirring for twelve hours. The alcohol was driven off from a water bath, water was added to the residue, and the oil formed was extracted with chloroform. The chloroform solution was washed with water and dried with calcium chloride. The product was 62 g (72.5%) of 8,8,8-trichlorooctane-

nitrile, b.p. 123-125° (2.5 mm); n_D^{20} 1.4787; d_4^{20} 1.2097; found MR 53.53; calculated MR 53.56.

Found %: N 6.18; 6.28

$C_8H_{12}Cl_3N$. Calculated %: N 6.12

Hydrolysis of 8,8,8-trichlorooctanenitrile. A solution of 15 g of 8,8,8-trichlorooctanenitrile in 30 ml of concentrated hydrochloric acid was heated with stirring in a boiling water bath for one hour. Water (30 ml) was added, and the solution was boiled under reflux for 30 minutes. On cooling, the solution yielded a precipitate of suberic acid, which was washed on the filter with cold water. The yield of acid, m.p. 139-140°, was 10.7 g (94%).

8,8,8-Trichlorooctanoic acid. A solution of 23 g of 8,8,8-trichlorooctanenitrile in a mixture of 80 ml of glacial acetic acid, 30 ml of concentrated hydrochloric acid, and 20 ml of water was heated under reflux for ten hours. The usual treatment yielded 19.6 g (79%) of 8,8,8-trichlorooctanoic acid, b.p. 139-140° (1.0 mm); m.p. 38-39° (from petroleum ether).

Found %: C 38.94; 39.02; H 5.37; 5.20

$C_8H_{13}O_2Cl_3$. Calculated %: C 38.82; H 5.25

The anilide of 8,8,8-trichlorooctanoic acid melts at 108-109°.

Found %: N 4.22; 4.33

$C_{14}H_{18}Cl_3NO$. Calculated %: N 4.34

4,4-Dichloro-3-butenoic acid was prepared as previously described [7].

The anilide of 4,4-dichloro-3-butenoic acid melts at 82-83°.

Found %: N 6.15; 6.18

$C_{10}H_9Cl_2NO$. Calculated %: N 6.08

5,5-Dichloro-4-penten-1-ol acetic ester. A solution of 65 g of 1,1,5-trichloro-1-pentene [4], 45 g of potassium acetate, and 1.5 g of potassium iodide in 150 ml of glacial acetic acid was heated under reflux for 16 hours. Water was added to the mixture, when cool, and the oil formed was extracted with chloroform. The chloroform solution was washed with a solution of sodium carbonate and dried with sodium sulfate. The product was 62.1 g (84%) of the acetic ester of 5,5-dichloro-4-penten-1-ol, b.p. 58° (1.5 mm); n_D^{20} 1.4690; d_4^{20} 1.2095; found MR 45.35; calculated MR 45.54.

Found %: C 42.83; 42.87; H 5.18; 5.42

$C_7H_{10}Cl_2O_2$. Calculated %: C 42.69; H 5.08

5,5-Dichloro-4-penten-1-ol. A solution of 53 g of the acetic ester of 5,5-dichloro-4-penten-1-ol and 1 ml of concentrated hydrochloric acid in 80 ml of methanol was heated under reflux for six hours. The methanol and methyl acetate were distilled off from a water bath, and 1 ml of concentrated hydrochloric acid and 60 ml of methanol were added to the residue. The solution was heated for a further three hours, and yielded 38 g (93%) of 5,5-dichloro-4-penten-1-ol, b.p. 59-60° (2.5 mm); n_D^{20} 1.4923; d_4^{20} 1.2452; found MR 36.14; calculated MR 36.18.

Found %: C 38.91; 38.95; H 5.22; 5.19

$C_5H_8Cl_2O$. Calculated %: C 38.75; H 5.16

5,5-Dichloro-4-pentenoic acid. A solution of 23.5 g of the diethyl ester of (3,3-dichloroallyl)malonic acid in a mixture of 70 ml of glacial acetic acid, 25 ml of concentrated hydrochloric acid, and 25 ml of water was boiled under reflux for eight hours. The mixture was cooled, water was added, and the oil formed was extracted with chloroform. The chloroform was distilled off from a water bath, and the residue was heated at 170-180° until evolution of carbon dioxide ceased (30 minutes), and was then dissolved in dilute caustic potash solution. The alkaline solution was extracted with ether and then acidified with hydrochloric acid. The oil that separated was extracted with chloroform. The chloroform solution was washed with water and dried with calcium chloride. After removal of chloroform, the residue was vacuum-distilled in a current of nitrogen, when it yielded 10.6 g (72%) of 5,5-dichloro-4-pentenoic acid, b.p. 93-94° (1 mm); n_D^{20} 1.4898; d_4^{20} 1.3546; found MR 36.06; calculated MR 3609.

Found %: C 35.61; 35.64; H 3.56; 3.59.

$C_5H_6Cl_2O_2$. Calculated %: C 35.52; H 3.55

The anilide of 5,5-dichloro-4-pentenoic acid melts at 72-73° (from benzene-ligroin).

Found %: N 5.60; 5.50

$C_{11}H_{11}Cl_2NO$. Calculated %: N 5.73

6,6-Dichloro-5-hexenoic acid was prepared in 92% yield by hydrolysis of the corresponding nitrile [5] with a mixture of acetic and hydrochloric acids; b.p. 139-140° (8 mm); n_D^{20} 1.4895; d_4^{20} 1.2967; found MR 40.77; calculated MR 40.71.

	Found %	C 39.17; 39.10; H 4.29; 4.34
$C_8H_8Cl_2O_2$.	Calculated %	C 39.32; H 4.37

The anilide of 6,6-dichloro-5-hexenoic acid melts at 63-64° (from benzene-ligroin).

	Found %	N 5.60; 5.45
$C_{12}H_{13}Cl_2NO$.	Calculated %	N 5.42

Diethyl ester of 5,5-dichloro-4-pentenylmalonic acid. 1,1,5-Trichloro-1-pentene (37g) was heated for ten hours with sodiomalonic ester prepared from 35 g of malonic ester and 4.7 g of sodium in 60 ml of absolute alcohol. When the mixture was cool, water was added, and the oil that separated was extracted with chloroform. The product was 37.2 g (60%) of the diethyl ester of 5,5-dichloro-4-pentenylmalonic acid, b.p. 122-123° (1.5 mm); n_D^{20} 1.4650; d_4^{20} 1.1693; found MR 70.22; calculated MR 70.19.

	Found %	C 48.75; 48.60; H 6.04; 6.04
$C_{12}H_{18}Cl_2O_4$.	Calculated %	C 48.50; H 6.06

7,7-Dichloro-6-heptenoic acid was obtained in 90% yield by hydrolysis of the diethyl ester of 5,5-dichloro-4-pentenylmalonic acid with a mixture of acetic and hydrochloric acids, the procedure being similar to that used for the preparation of 5,5-dichloro-4-pentenoic acid, b.p. 120-121° (1 mm); n_D^{20} 1.4872; d_4^{20} 1.2479; found MR 45.41; calculated MR 45.33.

	Found %	C 42.71; 42.62; H 5.02; 4.92
$C_7H_{10}Cl_2O_2$.	Calculated %	C 42.64; H 5.07

The anilide of 7,7-dichloro-6-heptenoic acid melts at 68-69° (from benzene-ligroin).

	Found %	N 5.19; 5.22
$C_{14}H_{15}Cl_2NO$.	Calculated %	N 5.14

8,8-Dichloro-7-octenenitrile. Heating of 30 g of 1,1,7-trichloro-1-heptene with 11 g of sodium cyanide in 70 ml of alcohol and 20 ml of water for twelve hours yielded 21.1 g (73%) of 8,8-dichloro-7-octenenitrile, b.p. 99-100° (1.5 mm); n_D^{20} 1.4840; d_4^{20} 1.1410; found MR 48.04; calculated MR 48.23.

	Found %	N 7.14; 7.12
$C_8H_{11}Cl_2N$.	Calculated %	N 7.29

8,8-Dichloro-7-octenoic acid was prepared in 80% yield by hydrolysis of 8,8-dichloro-7-octenenitrile with a mixture of acetic and hydrochloric acids; b.p. 128-129° (1 mm); n_D^{20} 1.4859; d_4^{20} 1.2120; found MR 49.97; calculated MR 50.04.

	Found %	C 45.66; 45.74; H 5.85; 5.90
$C_8H_{12}Cl_2O_2$.	Calculated %	C 45.52; H 5.68

The anilide of 8,8-dichloro-7-octenoic acid melts at 62-63° (from benzene-ligroin).

	Found %	N 4.97; 5.01
$C_{14}H_{17}Cl_2NO$.	Calculated %	N 4.89

Diethyl ester of 7,7-dichloro-6-heptenylmalonic acid. 1,1,7-Trichloro-1-heptene (40 g) was heated for ten hours with sodiomalonic ester prepared from 35 g of malonic ester and 4.6 g of sodium in 70 ml of absolute alcohol. The product was 41.1 g (65%) of the diethyl ester of 7,7-dichloro-6-heptenylmalonic acid, b.p. 142-143° (1 mm); n_D^{20} 1.4663; d_4^{20} 1.1341; found MR 79.41; calculated MR 79.43.

	Found %	C 51.44; 51.40; H 6.63; 6.59
$C_{14}H_{22}Cl_2O_4$.	Calculated %	C 51.69; H 6.76

9,9-Dichloro-8-nonenoic acid was prepared in 82% yield by hydrolysis of the diethyl ester of 7,7-dichloro-6-heptenylmalonic acid with a mixture of acetic and hydrochloric acids, the procedure being similar to that used for the preparation of 5,5-dichloro-4-pentenoic acid; b.p. 132-133° (1 mm); n_D^{20} 1.4848; d_4^{20} 1.1806; found MR 54.60; calculated MR 54.68.

	Found %	C 47.91; 47.89; H 6.23; 6.17
$C_9H_{14}Cl_2O_2$.	Calculated %	C 48.00; H 6.22

The anilide of 9,9-dichloro-8-nonenoic acid melts at 54-55° (from benzene-ligroin).

Found % N 4.77; 4.63

$C_{15}H_{19}Cl_2NO$. Calculated % N 4.66

SUMMARY

1. The acids $CCl_3(CH_2)_nCOOH$ (n = 2-6) and $CCl_2=CH-(CH_2)_nCOOH$ (n = 1-6) have been prepared, and their dissociation constants have been measured potentiometrically.

2. It has been found that the CCl_3 and $CCl_2=CH$ groups have appreciable effects on the dissociation constants of the acids; these effects fall off regularly as the length of the chain separating these groups from carboxyl increases.

3. It has been found that 4,4-dichloro-3-butenoic acid has a higher dissociation constant that 4,4,4-trichlorobutyric acid, whereas in the succeeding acids in the two series the reverse relationship holds.

4. It has been found that in the higher ω,ω,ω-trihalo carboxylic acids, the CCl_3 and CF_3 groups have approximately the same effect on the dissociation constant.

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Institute of Heteroorganic Compounds
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REACTIONS OF ORGANOMAGNESIUM COMPOUNDS WITH POTASSIUM AND TRIETHYLOXONIUM FLUOBORATES

A. N. Nesmeyanov, V. A. Sazonova, G. S. Liberman and L. I. Emelyanova

For the synthesis of full organoboron compounds, it has been usual to apply the reaction of organomagnesium compounds with boric esters or halogen derivatives of boron. Of the boron halides, the trifluoride is the most frequently used (in the form of its etherate). It is known that inorganic and organic boron derivatives tend to form complexes. Recently, Wittig and coworkers [1] have shown that in ether solution triphenylborine combines with phenyllithium:

$$(C_6H_5)_3B + C_6H_5Li \rightarrow LiB(C_6H_5)_4.$$

Lithium tetraphenylboron can be obtained also by the action of BF_3 on C_6H_5Li. For purposes of analysis the authors used the reaction of lithium tetraphenylboron with mercuric chloride, which goes quantitatively with formation of C_6H_5HgCl, HCl, H_3BO_3, and LiCl. When a potassium salt is added to an aqueous solution of $LiB(C_6H_5)_4$, the water-insoluble potassium tetraphenylboron is formed:

$$LiB(C_6H_5)_4 + K^+ \rightarrow KB(C_6H_5)_4 + Li^+.$$

When lithium tetraphenylboron is treated with cupric chloride (in equimolecular amount), the salt is decomposed with formation of biphenyl and triphenylborine. When a large excess of lithium tetraphenylboron is used, copper tetraphenylboron is obtained. The reaction is carried out in ether solution over a period of a week. Compounds of the type MBR_4 have as yet received little study, and such work as has been done has been largely confined to the phenyl derivative.

In the present paper we propose a simpler and more convenient method for the synthesis of trimethylborine and certain tetraarylboron salts. It has been found that potassium tetraphenylboron is readily prepared in ether by the action of phenylmagnesium bromide on potassium fluoborate:

$$4C_6H_5MgBr + KBF_4 \rightarrow KB(C_6H_5)_4 + 4MgBrF.$$

Reaction with p-tolylmagnesium bromide is somewhat more difficult.

In comparison with $KB(C_6H_5)_4$, potassium tetra-p-tolylboron is considerably less soluble in organic solvents (acetone, chloroform, and pyridine). Both the tetraphenyl and the tetratolyl compounds have high thermal stability. Thus, they do not decompose even when heated to 300-350°. Their decomposition with mercuric chloride (in acetone) with elimination of aryls in the form of the corresponding organomercury compound confirms the presence of four aryl groups in the substances obtained.

Potassium tetraphenylboron reacts in pyridine solution with the copper derivative of acetoacetic ester (when warmed for a few minutes), and yields a double compound of pyridine (pyridinate) with a copper tetraphenylboron containing a univalent copper atom.

$CuB(C_6H_5)_4 \cdot 4C_5H_5N$ is a light-yellow powder, which is converted by careful acidification into cuprous tetraphenylboron, a colorless substance of low stability.

The pyridinate of cuprous tetraphenylboron is comparatively stable: after being kept for several days, no signs of decomposition can be detected.

Under similar conditions (by the action of the copper derivative of acetoacetic ester on potassium tetra-p-tolylboron), we have prepared the pyridinate of copper tetra-p-tolylboron, which, unlike the phenyl compound, is very unstable. It crystallizes with three molecules of pyridine, and a few hours after its preparation an odor of pyridine appears and the substance darkens. Under the conditions described above it was not found possible to isolate copper tetratolylboron without combined pyridine: when an attempt was made to eliminate pyridine by means of dilute H_2SO_4, p,p'-bitolyl and metallic copper were obtained.

Potassium tetratolylboron reacts with bromine with formation mainly of bitolyl, which is an indication of the radical nature of the reaction, since an ionic mechanism would be expected to result in the formation of p-bromo-

toluene. Razuvaev and Brilkina [2] have shown that the compounds MBR_4 can undergo decomposition of the radical type; thus, agitation of $KB(C_6H_5)_4$ with mercury in chloroform for 70-80 hours resulted in the formation of diphenylmercury.

By no means all organomagnesium compounds react with potassium fluoborate to yield stable compounds of the type KBR_4. Thus, with methylmagnesium iodide and with p-methoxyphenylmagnesium bromide potassium fluoborate yields trimethylborine and tris-p-methoxyphenylborine, respectively. It may be supposed, however, that in these cases also compounds of the type KBR_4 are formed as intermediate compounds, but they are unstable and decompose. We carried out the reaction of methylmagnesium iodide with potassium fluoborate in ether in an atmosphere of nitrogen and then decomposed the reaction complex with water. Trimethylborine then separated and was identified in the form of its ammoniate. In the direct reaction between CH_3MgI and KBF_4 without addition of water, no trimethylborine separates – a fact that supports the idea of the intermediate formation of $KB(CH_3)_4$ decomposed by water with formation of $(CH_3)_3B$.

There are indications in the literature of the formation of tetraalkylboron salts. Schlesinger and Brown [3] have carried out the reaction between ethyllithium and trimethylborine, and they consider that they have obtained $Li[B(CH_3)_3C_2H_5]$, stable to dry air, but decomposed by water with evolution of gas. Somewhat later, lithium tetramethylboron was described [4]. The reaction between methylmagnesium iodide and potassium fluoborate provides a convenient method for the preparation of trimethylborine, since it makes it unnecessary to work with boron trifluoride.

It is interesting that triethyloxonium fluoborate reacts like potassium fluoborate with phenylmagnesium bromide:

$$(C_2H_5)_3O^+BF_4 + 4C_6H_5MgBr \rightarrow (C_2H_5)_3O^+B(C_6H_5)_4 + 4MgBrF.$$

The reaction proceeds with a yield of 30% of oxonium salt when an ether solution of the organomagnesium compound is added to triethyloxonium fluoborate. Triethyloxonium tetraphenylboron can be obtained in good yield also from $KB(C_6H_5)_4$ and $(C_2H_5)_3O^+BF_4$:

$$KB(C_6H_5)_4 + (C_2H_5)_3O^+BF_4 \rightarrow (C_2H_5)_3O^+B(C_6H_5)_4 + KBF_4.$$

Triethyloxonium tetraphenylboron is stable in the air, and is insoluble in water, but soluble in nitrobenzene; it melts at 115-116°. Like other oxonium salts it is an alkylating agent; thus it converts picric acid into ethyl picrate.

EXPERIMENTAL

Potassium Tetraphenylboron

To 4 g of KBF_4 80 ml of an ether solution of C_6H_5MgBr at a concentration of 0.27 g per ml was added. Reaction, accompanied by evolution of heat, began after a few minutes. The mixture was well-stirred, and reaction was complete in 2-3 hours. The mixture was poured into an ammonium chloride solution, and a precipitate separated that was insoluble both in water and in ether. It was filtered off, washed several times with water and ether, and dissolved in acetone. The acetone solution was filtered from unchanged KBF_4 and water was added. The precipitate that formed was filtered off and washed with water and ether. The yield of potassium tetraphenylboron was 8 g (70%).

Analysis for potassium was carried out as follows: to a weighed amount of the substance 25 ml of 0.1 N HCl and some ether were added (in absence of ether, dissolution is very slow), and when solution was complete the excess of HCl was titrated with alkali.

	Found %	C 80.34; 80.51;	H 5.64; 5.74;	K 11.10
$C_{24}H_{20}BK$	Calculated %	C 80.44;	H 5.60;	K 10.91

The substance is soluble in cold acetone and in cold pyridine, but less soluble in hot acetone and in hot pyridine.

Potassium Tetra-p-tolylboron

Potassium fluoborate (1.44 g) was added to p-tolylmagnesium bromide prepared from 8 g of p-bromotoluene and 1.1 g of magnesium in 50 ml of ether. The reaction mixture was heated for three hours in a water bath with constant vigorous stirring, and was then poured into an ammonium chloride solution. At the interface between the aqueous and ethereal layers, a precipitate formed. The ether layer was separated together with the precipitate and was washed several times with water. The precipitate was filtered off, washed with ether, and dried, when 1.87 g of unpurified product was obtained. The potassium tetratolylboron was purified by dissolving it in acetone, filtering the turbid solution, and adding water. The resulting precipitate was filtered off and washed with water and ether. The yield was 32% on the amount of KBF_4 taken for reaction.

Found %: C 81.33; 81.39; H 7.26; 7.21; K 9.48

$C_{28}H_{25}BK$. Calculated %: C 81.15; H 6.81; K 9.41

Potassium tetratolylboron can be purified by adding cyclohexane to the acetone solution instead of water. Potassium tetratolylboron is insoluble in water and sparingly soluble in organic solvents.

Cuprous Tetraphenylboron

1) The copper derivative of acetoacetic ester (0.11 g) was added to 0.25 g of potassium tetraphenylboron in 10 ml of pyridine. The green solution was heated cautiously for a few minutes in a water bath until its color changed from green to dark brown. When the solution was cold, water was added, and the resulting precipitate was filtered off and washed with 1:1 aqueous pyridine and with water. The product was 0.23 g (96%) of the yellow pyridinate of cuprous tetraphenylboron.

Found %: C 75.63; H 5.86; N 8.04; 7.83

$C_{44}H_{40}N_4BCu$. Calculated %: C 75.68; H 5.77; N 8.04

2) Dilute sulfuric acid was added to an aqueous suspension of 0.22 g of $CuB(C_6H_5)_4 \cdot 4C_5H_5N$, and as the mixture was stirred the suspended solid turned from yellow to white. The cuprous tetraphenylboron was filtered off and washed with water. The yield was quantitative. The substance decomposed at 72-73°, and when exposed to the air it darkened fairly rapidly and an odor of biphenyl developed.

Found %: C 75.18; H 5.68

$C_{24}H_{20}BCu$. Calculated %: C 75.29; H 5.27

Cuprous Tetra-p-tolylboron

The copper derivative of acetoacetic ester (0.1 g) was added to 0.2 g of potassium tetra-p-tolylboron in 15 ml of pyridine. The mixture was carefully heated with constant agitation until the solution became clear and changed in color from green to dark brown, which required a few minutes. When the solution was cold, water was added, and the resulting precipitate was filtered off and washed with 1:1 aqueous pyridine, water, and low-boiling petroleum ether. The product was 0.12 g (67%) of $CuB(C_6H_4CH_3)_4 \cdot 3C_5H_5N$.

Found %: C 76.39; 76.48; H 6.26; 6.36; N 6.15

$C_{43}H_{43}N_3BCu$. Calculated %: C 76.38; H 6.41; N 6.22

The substance decomposed with storage. It was not found possible to isolate cuprous tetratolylboron without combined pyridine under the conditions of the previous experiment: p,p'-bitolyl and metallic copper were obtained.

Decomposition of Potassium Tetraphenylboron with Mercuric Chloride

To a solution of 0.1224 g of $KB(C_6H_5)_4$ in acetone, a little water was added, and then an acetone solution of 0.5 g of $HgCl_2$. There was an immediate precipitate of phenylmercury chloride. In order to complete the decomposition of the organoboron compound, the mixture was heated in a water bath, and the acetone was driven off. The phenylmercury chloride was filtered off and washed with water. The product was 0.41 g (95%) of C_6H_5HgCl, m.p. 252°. A mixture with authentic phenylmercury chloride melted at the same temperature.

Decomposition of Potassium Tetra-p-tolylboron with Mercuric Chloride

An acetone solution of 0.4 g (38% excess) of mercuric chloride was added to a solution of 0.1108 g of potassium tetra-p-tolylboron in acetone, and a few drops of water were added. The acetone was then slowly distilled off. When about one-quarter of the solvent remained in the flask, the condenser was set for reflux and the solution was heated for 30 minutes in a water bath. When the mixture was cool, water was added, and the precipitate of p-tolylmercury chloride was filtered off, washed with water, and dried. The product was 0.3166 g (94%) of p-tolylmercury chloride. It was recrystallized from benzene; m.p. 236-236.5°. A mixture with authentic p-tolylmercury chloride melted at 236-237°.

Action of Bromine on Potassium Tetra-p-tolylboron

A solution of dry bromine in chloroform was added to 1 g of potassium tetra-p-tolylboron in 10 ml of chloroform at room temperature with stirring until decolorization ceased to occur. Water was then added in order to dissolve the precipitated KBr. The chloroform layer was separated, washed with water, with 10% NaOH, and again with water, and then dried with $CaCl_2$. The chloroform was evaporated off, and the residue was recrystallized from alcohol, when 0.21 g (95%) of p,p'-bitolyl, m.p. 121°, was obtained. When this reaction was carried out in water —with bromine water under similar conditions— p,p'-bitolyl was again obtained, and in addition p-bromotoluene (identified in the form of p-toluic acid) was formed.

Action of Methylmagnesium Iodide on Potassium Fluoborate

Methylmagnesium iodide was prepared from 3 g of magnesium in 40 ml of absolute ether and 19 g of methyl iodide in 20 ml of ether in a flask fitted with a tube for the passage of nitrogen and a two-way adapter carrying a dropping funnel and a reflux condenser. The reaction was carried out in a current of pure dry nitrogen, and the apparatus was protected from access of moisture with the aid of a vessel containing sulfuric acid. When reaction was complete, the solution of methylmagnesium iodide was decanted in a current of nitrogen from the unchanged magnesium into a similar flask fitted with a tube for the passage of nitrogen, a dropping funnel, and a reflux condenser. Potassium fluoborate (3.4 g) was added; reaction began immediately, and the ether came to the boil. When reaction was complete, the sulfuric acid vessel was replaced by one containing strong aqueous ammonia cooled with ice. The reaction mixture was then decomposed by careful, dropwise addition of water from the dropping funnel. A liquid layer of the ammoniate of trimethylborine collected above the ammonia solution; it was separated from the aqueous layer and placed in a desiccator over sulfuric acid, where it solidified in the form of colorless crystals. The product was 1.23 g (62%) of trimethylborine ammoniate, m.p. 56°. The literature gives m.p. 56° [5, 6], but by the use of carefully purified trimethylborine and gaseous ammonia an ammoniate of m.p. 73.2-73.7° has been obtained [7].

Action of p-Methoxyphenylmagnesium Bromide on Potassium Fluoborate

Potassium fluoborate (1.44 g) was added to a solution of p-methoxyphenylmagnesium bromide prepared from 1.1 g of magnesium in 30 ml of absolute ether and 8.56 g of p-bromoanisole in 20 ml of absolute ether. The reaction mixture was heated in a water bath for three hours with constant vigorous stirring, after which it was poured into an ammonium chloride solution. The ether layer was separated and washed with water, and concentrated aqueous ammonia was then added. The mixture was shaken, and a precipitate formed at the interface between the aqueous and ethereal layers, it was filtered off and washed with water and ether. The product was 0.57 g (14%) of the ammoniate of tris-p-methoxyphenylborine, m.p. 185-189°; after recrystallization from alcohol it melted at 190°.

	Found %	N 3.98
$C_{21}H_{24}O_3NB$.	Calculated %	N 4.02

Triethyloxonium Tetraphenylboron

1. Double decomposition of potassium tetraphenylboron with triethyloxonium fluoborate. A freshly prepared solution of 1.3 g of $(C_2H_5)_3OBF_4$ [8] in acetone (when allowed to stand for a few minutes in acetone, triethyloxonium fluoborate decomposes) was added to 2.1 g of $KB(C_6H_5)_4$ dissolved in the least possible amount of acetone. A precipitate formed immediately and was rapidly filtered off (if it is left under acetone it decomposes); it was washed with a small amount of acetone. The product was 2.85 g of a mixture of $(C_2H_5)_3O^+B(C_6H_5)_4$ and KBF_4. In order to purify it from KBF_4 the substance was dissolved in nitrobenzene; the solution obtained was filtered, and precipitation with absolute ether yielded 1.8 g (73%) of triethyloxonium tetraphenylboron, m.p. 115-116°.

	Found %	C 85.15; 85.01; H 8.44; 8.77
$C_{26}H_{35}OB$.	Calculated %	C 85.29; H 8.35

2. Action of phenylmagnesium bromide on triethyloxonium fluoborate. An ether solution of C_6H_5MgBr (10 ml; concentration 0.394 g per ml) was added gradually to 1 g of $(C_2H_5)_3O^+BF_4$ in 15 ml of absolute ether; there was a vigorous reaction. The reaction mixture was stirred for a few minutes and poured into an ammonium chloride solution. The resulting precipitate, which was insoluble in water and in ether, was filtered off and washed with water and ether. It was dissolved for purification in nitrobenzene, the resulting solution was filtered, and the oxonium salt was precipitated with ether. The product was 0.67 g (30%) of triethyloxonium tetraphenylboron, m.p. 115-116°. In admixture with the preparation described in the previous experiment it showed no melting point depression.

3. Alkylation with triethyloxonium tetraphenylboron. Triethyloxonium tetraphenylboron (0.1 g) and picric acid (0.6 g) were heated with pure acetone until solution was complete. The reaction mixture was poured into water, and the ethyl picrate was extracted with ether, the extract being washed several times with water to remove picric acid. The ether was evaporated, and the residue was recrystallized from alcohol, and yielded 0.03 g of ethyl picrate, which melted after recrystallization from alcohol at 77-78°. A mixture with authentic ethyl picrate melted at the same temperature.

SUMMARY

1. A study has been made of the reaction of potassium fluoborate with organomagnesium compounds, namely phenylmagnesium, p-tolylmagnesium and p-methoxyphenylmagnesium bromides and methylmagnesium iodide. In the first two cases, the products were potassium tetraphenylboron and potassium tetra-p-tolylboron, respectively.

whereas p-methoxyphenylmagnesium bromide and methylmagnesium iodide yielded tris-p-methoxyphenylborine, and triphenylborine, respectively.

2. By reaction in pyridine of the copper derivative of acetoacetic ester with potassium tetraphenylboron and with potassium tetra-p-tolylboron the pyridinates of cuprous tetraphenylboron and cuprous tetra-p-tolylboron were obtained.

3. By reaction with phenylmagnesium bromide, and also with potassium tetraphenylboron, triethyloxonium fluoborate yields triethyloxonium tetraphenylboron.

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M. V. Lomonosov Moscow State University

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REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 1. 3,3-DIMETHYLISOCYSTEINE AND ITS DERIVATIVES

I. L. Knunyants, M. G. Linkova, and P. G. Ignatenok

In recent years, owing to advances made in chemistry and biochemistry, the exceptional importance of sulfur-containing organic compounds in animal physiology is becoming more and more evident. The greatest significance is to be assigned to compounds containing the thiol group, particularly mercapto amino acids, which enter into the composition of a large number of specific proteins and enzymes. Thus, cysteine and glutathione retard the clotting of the blood and play a determining part in the regulation of certain oxidation-reduction processes. Methionine appears to be the only carrier of methyl groups for a series of compounds synthesized in the organism; its importance will be realized when it is remembered that it is an essential element in the diet of animals and is for that reason manufactured on the industrial scale.

Glutathione and cysteine, together with ascorbic acid, inhibit the activity of certain toxins (diphtherial); also they enter into the composition of insulin, and they have been applied with success in the treatment of certain forms of diabetes. It is probable that an essential part is played in the organism by other thiol compounds, such as coenzyme A, which is responsible for the acetylation of choline and phosphorylation of adenosine phosphates; it has been shown to contain 2-aminoethanethiol (decarboxylation product of cysteine), which in coenzyme A is attached by an amide linkage to pantothenic acid. The free thiol group of coenzyme A is the transmitter of the acetyl residue (via an ester of thiolacetic acid). Glutathione, which has a number of functions, plays a part also in the reduction of oxidized forms of coenzyme A.

The significance of the thiol group in the transfer of the acetyl group is evidenced in recently established facts relating to the extremely high acetylating power of thiolacetic acid, which acetylates various substances in the cold, including amino acids in aqueous solution at a pH of about 7. The special part played by thiol compounds can be seen also from the breakdown that occurs in physiological processes when substances capable of blocking thiol groups act upon the organism. Thus, the effects due to chloroarsines and lachrymatories are generally known, and these have now been shown to depend, according to the structure of the inhibitor, either on the alkylation or on the acylation of the thiol groups of enzymes. Blocking of the hexokinases of the skin results in serious skin affections, and so on.

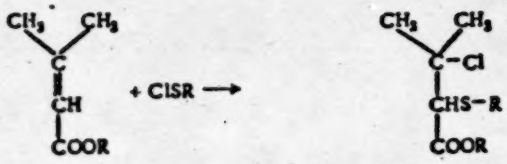
It is probable also that the antibiotic activity of many substances is associated with their ability to block the SH groups of the metabolites of bacteria. It has been found, for example, that penicillin has a high specificity in reactions with thiols. Other antibiotics containing double bonds conjugated with carbonyl are also able to combine with thiol-containing substances.

Penicillin, clavacin, streptomycin, bacitracin, and other antibiotics are inactivated by cysteine, glutathione, and BAL (2,3-dimercapto-1-propanol). The same occurs with unsaturated lactones, certain oxazolinones, and mixed anhydrides having antibiotic activity when they act selectively on certain thiol-containing compounds that are essential for cell metabolism. For this reason many mercapto amino acids and their derivatives have interesting physiological effects, and, although the mechanisms of these effects are not known in detail, it is clear that there are extensive opportunities for work in this field; particular interest is presented by those derivatives of mercapto amino acids that, owing to structural peculiarities, are reactive toward thiols.

Great interest is presented also by the elucidation of the biochemical role and action of those mercapto amino acids that are not indigenous to the organism and may be able to replace the metabolites. Thus, we have not yet determined the part played by dimethylcysteine, which can be obtained from penicillin and which, unlike other naturally occurring mercapto amino acids, is dextrorotatory. The action of the natural isomeric α-mercapto β-amino acids has not been elucidated at all; they have not been investigated owing to the fact that the only known member —isocysteine— has been obtained only in a minute amount by a complicated method.

In a series of investigations, the first of which is described in this paper, the authors have investigated a number of the reactions of β-mercapto α-amino acids and have effected the syntheses of some members of the isomeric series of α-mercapto β-amino acids.

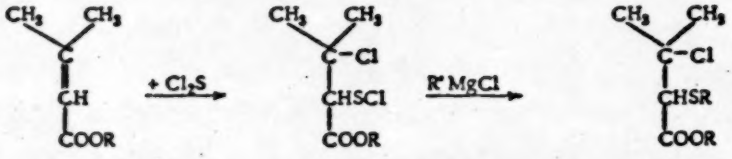
We have shown that alkanesulfenyl chlorides readily unite with unsaturated acids with formation of α-alkylthio β-chloro acids of the type:



(I)

In this way methane-, ethane-, α-toluene-, 2-chloroethane-, and 2-chloropropane-sulfenyl chlorides were caused to add to senecioic acid and its ethyl ester. The yields of the corresponding esters of 2-(alkylthio)-3-chloro-3-methylbutyric acids varied from 50% to 85%. In a number of cases, instead of the sulfenyl chlorides, the corresponding disulfides were taken for the reaction. In this variant of the method, a mixture of equimolecular amounts of the senecioic ester and the disulfide was treated with chlorine or sulfuryl chloride, when the nascent sulfenyl chloride formed immediately added at the double bond This method has an advantage in cases in which the sulfenyl chloride is unstable, as, for example, in the case of α-toluenesulfenyl chloride.

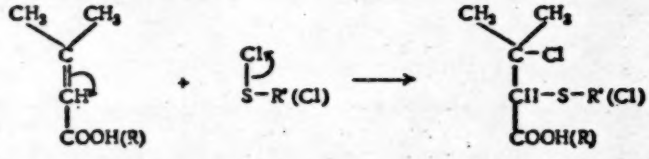
2-(Alkylthio)-3-chloro-3-methylbutyric acid and its derivatives can be obtained also from α-chlorothio β-chloro carboxylic acids by the action of alkylmagnesium halides. The ethyl ester of 3-chloro-2-(chlorothio)-3-methylbutyric acid (II) is obtained by the addition of sulfur dichloride to the ethyl ester of senecioic acid:



(II)

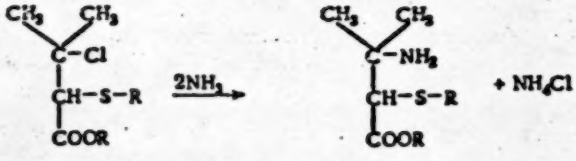
In this variant the fact that the reaction between sulfur dichloride and the unsaturated compound comes to a stop at the sulfenyl chloride stage is unprecedented: in all other cases, as is well-known, the reaction proceeds further and the corresponding sulfide is obtained. The resulting sulfenyl chloride (II) is stable, readily distils in a vacuum, and can be preserved for a long time without decomposition. The reaction of the sulfenyl chloride with benzylmagnesium chloride goes instantaneously and in quantitative yield. The resulting 2-(benzylthio)-3-chloro-3-methylbutyric ester is identical with the ester obtained by the reaction of dibenzyl disulfide with the ethyl ester of senecioic acid in presence of chlorine.

Thus, sulfur dichloride and alkanesulfenyl chlorides add to senecioic acid in the same direction, in accordance with the polarities of the original reactants:



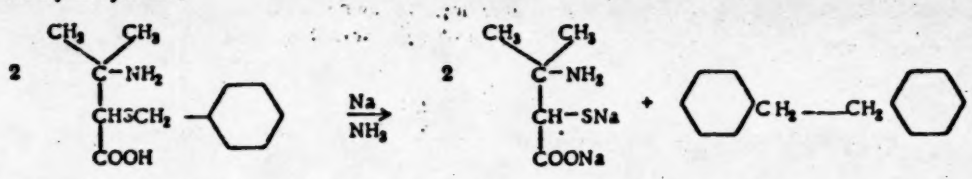
As would be expected in this case, introduction of peroxy compounds into the reaction medium does not affect the direction of the addition.

The resulting esters of 2-(alkylthio)-3-chloro-3-methylbutyric acids are readily converted into the corresponding esters of amino acids by keeping them for 10-12 hours in liquid ammonia in a closed vessel at room temperature:



After evaporation of the ammonia, which was completed in a current of dry air, the amino acid esters were separated from ammonium chloride by extraction with ether. The hydrochlorides of the amino acid esters were obtained by passage of hydrogen chloride through the ether extracts.

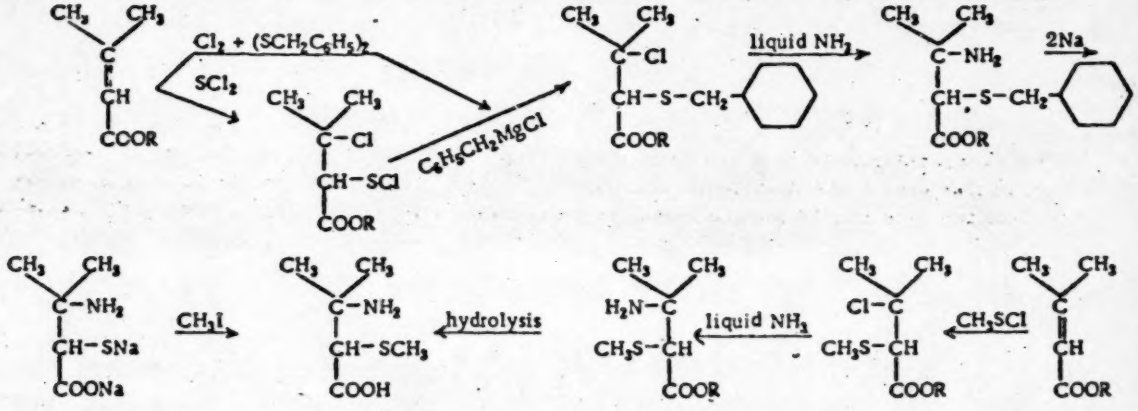
In no case was ammonolysis with formation of an amide observed, and the amino acid esters were obtained in 60-90% yield. The free amino acids were liberated by hydrolysis of the esters with 1:1 hydrochloric acid. S-Benzyl-3,3-dimethylisocysteine was debenzylated by means of sodium in liquid ammonia, and yielded the sodium salt of 3,3-dimethylisocysteine:



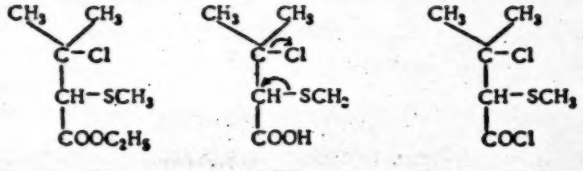
The direction of the addition of alkanesulfenyl chlorides and sulfur dichloride to senecioic acid and its ester was proved by comparison of the properties of the S-alkyl-3,3-dimethylisocysteines so obtained with those of the isomeric S-alkyl-3,3-dimethylcysteines synthesized by Savard [2] by the addition of thiols to 4-isopropylidene-2-phenyl-2-oxazolin-5-one.

Treatment of S-benzyl-3,3-dimethylisocysteine with sodium in liquid ammonia, followed by methylation with methyl iodide, yielded S-methyl-3,3-dimethylisocysteine, identical with the S-methyl-3,3-dimethylisocysteine synthesized by the addition of methanesulfenyl chloride to the ethyl ester of senecioic acid.

We give here a scheme illustrating the transformations effected:



In the course of our study of the addition products formed by sulfur chlorides with senecioic acid and its ester, a number of remarkable facts were noted. As already stated, methanesulfenyl chloride adds in similar fashion to senecioic acid and to its ester, forming the compounds (III) and (IV):



(IV) (III) (V)

The structure of the compound (IV) as a 3-chloro compound has been rigorously proved by us (above). The compound (III) is much less stable than (IV), and cannot be kept for a long time. When an attempt was made to esterify compound (III) with absolute alcohol in presence of hydrochloric acid, the ethyl ester of senecioic acid was obtained in quantitative yield. When it reacts with ammonia, (III) readily eliminates methanesulfenyl chloride and is converted into senecioic acid. The product of the addition of sulfur dichloride to senecioic acid behaves completely analogously: thus, when it is treated with ammonia, senecioic acid is readily regenerated.

On the basis of these transformations it might be concluded that (III) is a complex of methanesulfenyl chloride and senecioic acid. It is found, however, that when (III) is treated with thionyl chloride the acid chloride (V) of the corresponding acid is obtained, and this reacts normally with alcohol with formation of the ester (IV), which we obtained previously by the addition of methanesulfenyl chloride to the ester of senecioic acid. It is clear that 3-chloro-3-methyl-2-(methylthio)butyric acid is strongly polarized, as indicated in the structural formula (III).

EXPERIMENTAL

Ethyl ester of 3-chloro-3-methyl-2-(methylthio)butyric acid. Freshly prepared methanesulfenyl chloride (7.7 g) was added gradually to 9.3 g of the ethyl ester of senecioic acid ; the temperature rose to 40-45°. The mixture was set aside at room temperature until the following day. Vacuum distillation of the product yielded 16 g (70%) of the ethyl ester of 3-chloro-3-methyl-2-(methylthio)butyric acid, b.p. 81-83° (1.5 mm); n_D^{25} 1.491; d_4^{25} 1.118; found MR 54.53; calculated MR 54.84.

Found %: Cl 17.3; S 15.0
$C_8H_{15}O_2SCl$. Calculated %: Cl 16.9; S 15.2

By the same method the following were obtained:

ethyl ester of 3-chloro-2-(ethylthio)-3-methylbutyric acid (77% yield), b.p. 123-125° (15 mm).

Found %: Cl 15.5; S 15.6
$C_9H_{17}O_2SCl$. Calculated %: Cl 15.82; S 14.28;

ethyl ester of 3-chloro-2-(2-chloroethylthio)-3-methylbutyric acid (77% yield), b.p. 135-140° (17 mm).

Found %: Cl 26.82; S 12.74
$C_9H_{16}O_2SCl_2$. Calculated %: Cl 26.71; S 12.4;

ethyl ester of 3-chloro-2-(2-chloropropylthio)-3-methylbutyric acid (87% yield), b.p. 120-121° (1 mm); n_D^{25} 1.500; d_4^{25} 1.180; found MR 68.0; calculated MR 67.45.

Found %: Cl 26.57; S 14.3
$C_{10}H_{18}O_2SCl$. Calculated %: Cl 26.0; S 14.7.

3-Chloro-3-methyl-2-(methylthio)butyric acid. Freshly prepared methanesulfenyl chloride (4.1 g, i.e., 0.05 mole) was added gradually to a solution of 5 g (0.05 mole) of senecioic acid in 20 ml of dry carbon tetrachloride. The mixture was set aside at room temperature for 10-12 hours. The carbon tetrachloride was evaporated off under reduced pressure until crystallization began. Recrystallization of the precipitate from petroleum ether yielded 4.55 g (50%) of a substance of m.p. 73-75°.

Found %: Cl 19.2; S 17.3
$C_6H_{11}O_2SCl$. Calculated %: Cl 19.5; S 17.5

Ethyl ester of 2-(benzylthio)-3-chloro-3-methylbutyric acid. Dibenzyl disulfide (3.6 g), ethyl senecioate (3.83 g), and benzoyl peroxide (0.2 g) were added to a solution of 1 g of chlorine in 10 ml of carbon tetrachloride. The mixture was heated for two hours in a water bath. The solvent was driven off under reduced pressure, and the residue was distilled in a high vacuum. The product was 4.5 g (50%) of a substance of b.p. 134-136° (0.2 mm).

Found %: S 11.43; Cl 12.46
$C_{14}H_{19}O_2SCl$. Calculated %: S 11.17; Cl 12.39

3-Chloro-2-(chlorothio)-3-methylbutyric acid. Sulfur dichloride (30 g, i.e., 0.3 mole) was cooled to −5°, and senecioic acid (10 g, i.e., 0.1 mole) was added in portions. The mixture was set aside at room temperature until the next day. A precipitate of 5 g (25%) of yellowish crystals, m.p. 70-71°, formed.

Found %: Cl 35.4; S 16.0
$C_5H_8O_2Cl_2S$. Calculated %: Cl 35.0; S 15.7

Ethyl ester of 3-chloro-2-(chlorothio)-3-methylbutyric acid. Sulfur dichloride (15 g, i.e., 0.15 mole) was cooled to −5° and was stirred while gradual addition was made of 6.4 g (0.05 mole) of ethyl senecioate over a period of 15-20 minutes. The resulting mixture was set aside at room temperature until the next day. The excess of sulfur dichloride was driven off under reduced pressure from a water bath, and the residue was vacuum-distilled, when it yielded 10 g (87%) of the ethyl ether of 3-chloro-2-(chlorothio)-3-methylbutyric acid, b.p. 95-98° (1-2 mm), in the form of a mobile orange liquid of characteristic odor.

Found %: Cl 31.1; S 13.93; Cl 15.1 (iodometrically)
$C_7H_{12}O_2Cl_2S$. Calculated %: Cl 30.73; S 13.85; Cl 15.36

Ethyl ester of 2-(benzylthio)-3-chloro-3-methylbutyric acid. A solution of 5.8 g of the ethyl ester of 3-chloro-2-(chlorothio)-3-methylbutyric acid in 100 ml of absolute ether was cooled with ice water, and benzylmagnesium chloride (0.7 g Mg, 200 ml of absolute ether, 3.6 g of benzyl chloride) was added from a dropping funnel to the stirred solution. A white precipitate of magnesium chloride formed. When the addition was complete, the

mixture was allowed to stand for 30 minutes at room temperature; it was then washed free from $MgCl_2$ with water in a separating funnel. The ether solution was dried over calcium chloride, and the ether was driven off. Vacuum distillation of the residue yielded 4 g (60.4%) of product, b.p. 134-136° (0.2 mm).

Reduction of the ethyl ester of 3-chloro-2-(chlorothio)-3-butyric acid. The ethyl ester of 3-chloro-2-(chlorothio)-3-butyric acid (5 g) was dissolved in 250 ml of ether. The solution was transferred to a separating funnel, and 100 ml of acidified 5% potassium iodide solution was added in portions and the mixture shaken. As reaction proceeded, a considerable amount of iodine separated and the temperature rose appreciably; reaction was complete in 10-15 minutes. The iodine was removed by washing the mixture with a thiosulfate solution. The ether layer was separated and dried over calcium chloride; the ether was driven off under reduced pressure, and the residue was distilled in a high vacuum, when a quantitative yield (4 g) of the diethyl ester of 2,2'-dithiobis[3-chloro-3-methylbutyric acid], b.p. 173-175° (0.2 mm) was obtained.

Found %: Cl 18.5; S 16.7
$C_{14}H_{24}O_4Cl_2S_2$. Calculated %: Cl 18.18; S 16.3

Hydrochloride of the ethyl ester of S,3,3-trimethylisocysteine. The ethyl ester of 3-chloro-3-methyl-2-(methylthio)butyric acid (9 g) was introduced into 50 ml of liquid ammonia. The autoclave was closed, and the reaction mixture was allowed to stand until the next day at room temperature. The ammonia was allowed to evaporate off, and the residue was extracted with ether. The ether extract was washed with water and dried over potassium carbonate. Dry HCl was passed until an acid reaction to Congo red was obtained. A precipitate of the hydrochloride of the ethyl ester of S,3,3-trimethylisocysteine formed; it was dissolved for purification in a small amount of absolute alcohol; and absolute ether was added until a slight turbidity appeared. By the next day 7.7 g (80%) of a crystalline product, m.p. 118-120°, had formed.

Found %: Cl 15.8; S 13.8; N 6.11
$C_8H_{17}O_2NSCl$. Calculated %: Cl 15.6; S 14.0; N 6.16

By the same method the following were obtained:

hydrochloride of the ethyl ester of S-ethyl-3,3-dimethylisocysteine (67% yield), m.p. 70-71°,

Found %: Cl 14.1; N 6.0
$C_9H_{19}O_2NS \cdot HCl$. Calculated %: Cl 14.7; N 5.8;

hydrochloride of the ethyl ester of S-benzyl-3,3-dimethylisocysteine (60.7% yield), m.p. 167-168°,

Found %: Cl 11.9; N 4.5
$C_{14}H_{21}O_2NS \cdot HCl$. Calculated %: Cl 11.7; N 4.6;

hydrochloride of the ethyl ester of S-2-chloroethyl-3,3-dimethylisocysteine (60.5% yield), m.p. 115-116°,

Found %: Cl 12.71 (Volhard)
$C_9H_{18}O_2NSCl \cdot HCl$. Calculated %: Cl 13.08;

hydrochloride of the ethyl ester of S-2-chloropropyl-3,3-dimethylisocysteine (65.5% yield), m.p. 147-148°,

Found %: N 4.7; Cl 11.8 (Volhard)
$C_{10}H_{20}O_2NSCl \cdot HCl$. Calculated %: N 4.82; Cl 12.2

S-Benzyl-3,3-dimethylisocysteine. A mixture of 7.2 g (0.002 mole) of the hydrochloride of the ethyl ester of S-benzyl-3,3-dimethylisocysteine and 60 ml of diluted HCl (one part of acid sp.gr. 1.19 and one part of water) was heated over a gauze for four hours under reflux. The solution was filtered and evaporated to dryness on a water bath. The residue was dissolved in 20 ml of water and neutralized with bicarbonate to pH 5, when the free S-benzyl-3,3-dimethylisocysteine came down (m.p. 189-190° with decomposition). Recrystallization from water yielded 5 g (86%) of product, m.p. 192-193°. A mixture with S-benzyldimethylcysteine prepared by Savard's method melted at 175-176° with decomposition (14° depression).

Found %: N 6.1
$C_{12}H_{17}O_2NS$. Calculated %: N 5.9

S-Ethyl-3,3-dimethylisocysteine was obtained in 49% yield; m.p. 202-203°.

Found %: N 7.9
$C_7H_{15}O_2NS$. Calculated %: N 7.9

S,3,3-Trimethylisocysteine. a) A solution of 2.5 g of the hydrochloride of the ethyl ester of S,3,3-trimethylisocysteine in 1:1 hydrochloric acid was boiled for two hours under reflux. The solution was then evaporated to dryness, dissolved in 7 ml of water, and neutralized with bicarbonate to pH 5.6. The precipitate that formed was pressed off. Crystallization from water yielded 1 g (62.5%) of a substance of m.p. 210-212°.

Found %: N 8.52; S 19.5
$C_6H_{13}O_2NS$. Calculated %: N 8.58; S 19.7

b) S-Benzyl-3,3-dimethylisocysteine (2 g) was dissolved in 100 ml of liquid ammonia. The solution was stirred and 0.5 g of sodium was added in small portions. A blue coloration of the solution, permanent over ten minutes, indicated the end of the reaction. The excess of sodium was removed by addition of ammonium chloride (decolorization). Methyl iodide (1.2 g) was then added, and the mixture was set aside until the next day. The ammonia was removed, and the residue was dissolved in 7 ml of water. The bibenzyl was repeatedly extracted with ether, and the aqueous solution was acidified to pH 5.6. The precipitate was filtered off and recrystallized from water, when 0.5 g of a substance of m.p. 211-212° was obtained.

Hydrochloride of 3,3-dimethylisocysteine. The elimination of the benzyl group from S-benzyl-3,3-dimethylisocysteine was carried out as in the preceding experiments, the same quantities being used. To the aqueous solution obtained (10 ml), 100 ml of a saturated solution of mercuric chloride was added, and the mixture was shaken for one hour. The precipitated mercury derivative rapidly coagulated. The mixture was set aside until the next day, when the precipitate was pressed off, washed with water, and dissolved in 5 ml of 10% HCl. The solution was filtered, and mercury was precipitated with hydrogen sulfide. The solution was filtered and evaporated down, first under reduced pressure at room temperature, and then in a vacuum desiccator over NaOH. The resulting crystalline precipitate was very hygroscopic.

Found %: N 7.27
$C_5H_{12}O_2NSCl$. Calculated %: N 7.54

Acid chloride of 3-chloro-3-methyl-2-(methylthio)butyric acid. Thionyl chloride (11 g) was added to a solution of 7.5 g of 3-chloro-3-methyl-2-(methylthio)butyric acid in 40 ml of dry carbon tetrachloride, and the mixture was heated until the evolution of HCl and SO_2 ceased. The carbon tetrachloride was driven off, and the residue was fractionated, when it yielded 8.4 g (60%) of the acid chloride of 3-chloro-3-methyl-2-(methylthio)butyric acid, b.p. 71-72° (3 mm); n_D^{28} 1.514; d_4^{20} 1.225; found MR 48.57; calculated MR 47.93.

Found %: Cl 24.6; S 15.4
$C_6H_{10}OSCl_2$. Calculated %: Cl 35.3; S 15.9

Ethyl ester of 3-chloro-3-methyl-2-(methylthio)butyric acid. Absolute alcohol (5 ml) was added dropwise to 8.4 g of the acid chloride of 3-chloro-3-methyl-2-(methylthio)butyric acid; reaction occurred with evolution of heat. When the evolution of HCl ceased, the mixture was vacuum-fractionated, and yielded 5.6 g (67%) of a substance of b.p. 81-83° (1.5 mm). The ethyl ester of 3-chloro-3-methyl-2-(methylthio)butyric acid so prepared was identical in properties with the ester prepared by another method (see the first experiment).

Reaction of 3-chloro-3-methyl-2-(methylthio)butyric acid with ammonia. 3-Chloro-3-methyl-2-(methylthio)butyric acid (1.5 g) was introduced into 50 ml of liquid ammonia. The autoclave was closed and left for twelve hours at room temperature. The ammonia was evaporated off, and the residue was dissolved in 5 ml of water. The solution was acidified with hydrochloric acid, and the resulting precipitate was pressed off and washed with water. The product (0.4 g) melted at 63-65°, undepressed by admixture with senecioic acid.

Reaction of 3-chloro-3-methyl-2-(methylthio)butyric acid with ethanol. A solution of 3.6 g of 3-chloro-3-methyl-2-(methylthio)butyric acid in 20 ml of absolute ethanol was saturated with dry hydrogen chloride, and the mixture was set aside for twelve hours at room temperature. Fractionation yielded ethyl senecioate, b.p. 36-38° (15 mm).

SUMMARY

1. The addition reactions of sulfur dichloride and alkanesulfenyl chlorides with senecioic acid and its ethyl ester have been described.

2. It has been shown that, unlike the addition of sulfur dichloride to olefins (which leads to the formation of symmetrical sulfides), its addition to senecioic acid and its ethyl ester yields stable sulfenyl chlorides.

3. By treatment of the addition products with ammonia, 3,3-dimethylisocysteine (isomer of the naturally occurring 3,3-dimethylcysteine) and a number of its derivatives have been synthesized.

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[1] Gabriel, Ber., 38, 630 (1905).

[2] K. Savard, et. al., J. Can. Res., 24, No. 1, 28 (1946).

REACTIONS OF MERCAPTO AMINO ACIDS

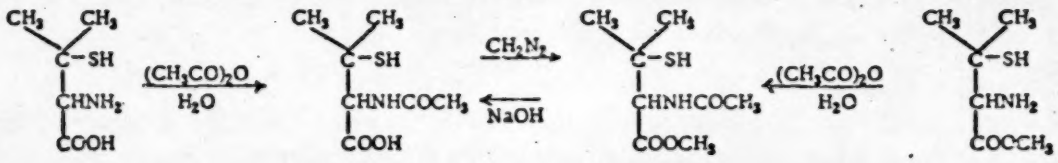
COMMUNICATION 2. ACYLATION AND ALKYLATION OF 3,3-DIMETHYLCYSTEINE

I. L. Knunyants and M. G. Linkova

3,3-Dimethylcysteine and its esters are readily acylated in an aqueous medium in presence of alkali. However, there is no proof that in all of these cases it is the amino group that is acylated; on the contrary, in view of the absence of reactions for the thiol group in acyl derivatives of 3,3-dimethylcysteine esters, the opposite conclusion might very well be reached.

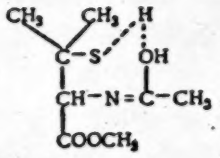
Acetylation of 3,3-dimethylcysteine with acetic anhydride or acetyl chloride yields an acetyl-3,3-dimethylcysteine of m.p. 182-183° (I) which gives a positive reaction for the thiol group. When an ester of 3,3-dimethylcysteine is acetylated, either with acetyl chloride in absolute ether or with acetic anhydride in water, in both cases the same acetyl derivative (II) of the ester is obtained, and this does not give a positive reaction with ferric chloride or sodium nitroprusside.

In order to determine the structures of these substances, the acetyl derivative of 3,3-dimethylcysteine was converted into its methyl ester by the action of diazomethane, and this was found to be identical with the product of the acetylation of the methyl ester of 3,3-dimethylcysteine:



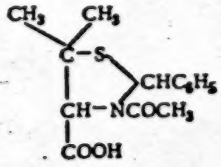
(I) (II)

Hydrolysis of this ester yielded the acetyl-3,3-dimethylcysteine of m.p. 182-183°. A mixture test with the product obtained by the acetylation of free 3,3-dimethylcysteine showed no depression. It was thus established that the acylation not only of 3,3-dimethylcysteine itself, but also of its esters occurs at a nitrogen atom. Absence of a reaction for the thiol group in esters of N-acyl derivatives of dimethylcysteine may arise from the formation of a strong intramolecular hydrogen bond (III):



(III)

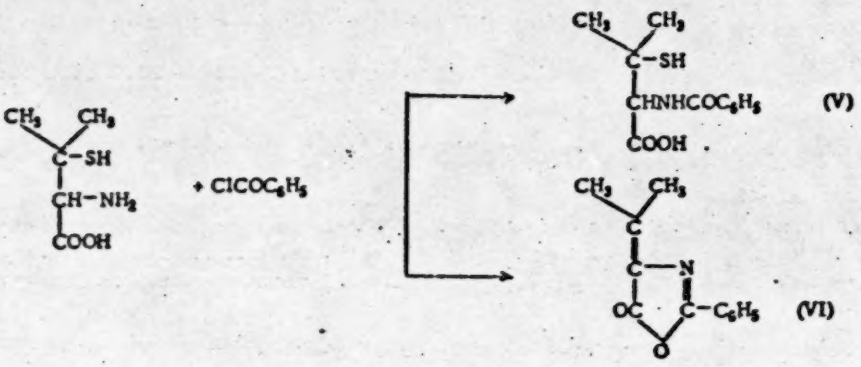
It is noteworthy that N-acetyl-3,3-dimethylcysteine reacts readily with benzaldehyde with formation of 3-acetyl-5,5-dimethyl-2-phenyl-4-thiazolinecarboxylic acid (IV) (m.p. 172-173° with decomposition):



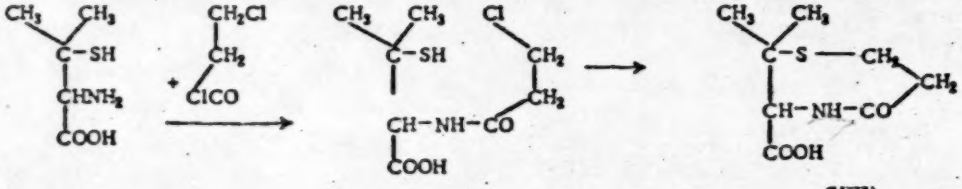
(IV)

whereas it is known that N-acyl derivatives of amines generally do not react with aldehydes [1].

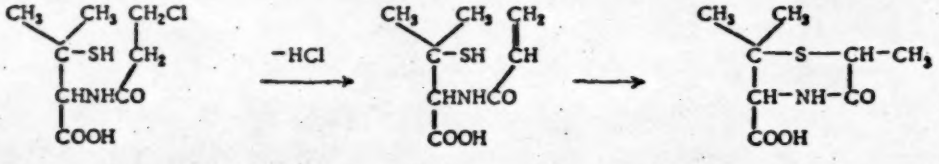
The benzoylation of 3,3-dimethylcysteine proceeds in a peculiar fashion: when the dimethylcysteine is treated with benzoyl chloride under Schotten-Baumann conditions, not only N-benzoyl-3,3-dimethylcysteine, but also 4-isopropylidene-2-phenyl-2-oxazolin-5-one (VI) is obtained in considerable amount:



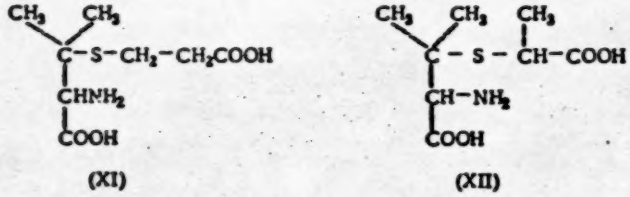
Phenylacetyl chloride reacts normally with 3,3-dimethylcysteine with formation of N-(phenylacetyl)-3,3-dimethylcysteine, m.p. 130-131°. 3,3-Dimethylcysteine and its ester reactiwith 3-chloropropionyl chloride with formation in high yield of N-(3-chloropropionyl)-3,3-dimethylcysteine (VII) and its ester respectively. When N-(3-chloropropionyl)-3,3-dimethylcysteine is treated with aqueous or alcoholic alkali, it is converted smoothly into the compound (VIII):



The structure (VIII), which contains a seven-membered ring, is open to some doubt, however, for apart from the alkylation reaction between the thiol group and the 3-chloropropionyl residue in (VII) with formation of (VIII), another possible reaction is not excluded, namely, the elimination of hydrogen chloride from the N-(β-chloropropionyl)-3,3-dimethylcysteine with formation of the intermediate compound (IX), and the subsequent addition of the thiol group with formation of the compound (X) containing a six-membered ring:



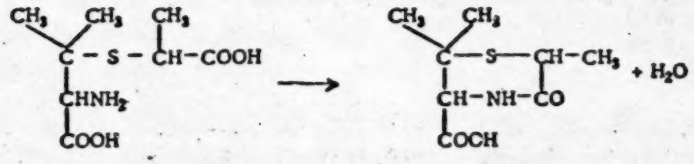
The question was resolved by a comparison of the hydrolysis products of (VIII) with synthetic amino acids obtained by the alkylation of 3,3-dimethylcysteine with 3-iodopropionic and 2-bromopropionic acids. Hydrolysis of (VIII) with a mixture of formic and hydrochloric acids yielded an amino acid, which, in correspondence with the structure (VIII) or the structure (X) could have one of the following structures:



The syntheses of these amino acids could be effected by determining the conditions for the S-alkylation of 3,3-dimethylcysteine. Experiment showed that 3,3-dimethylcysteine readily reacts with alkyl halides in an aqueous

medium at pH 8-9 with formation of S-alkyl derivatives. Thus, with methyl iodide and benzyl chloride quantitative yields were obtained of S-methyl- and S-benzyl-3,3-dimethylcysteine, which were found to be identical with the substances obtained by Savard and coworkers [2] by the alkylation of 3,3-dimethylcysteine with methyl iodide in liquid ammonia and the addition of α-toluenethiol to 4-isopropylidene-2-phenyl-2-oxazolin-5-one.

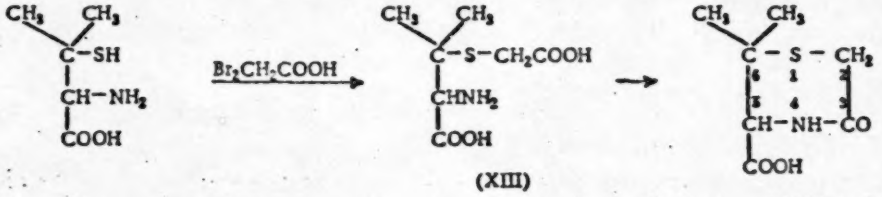
The extension of these reactions to 3-iodopropionic and 2-bromopropionic acids resulted in the preparation of two different amino acids, of which the product of the alkylation of 3,3-dimethylcysteine with 3-iodopropionic acid (S-(2-carboxyethyl)-3,3-dimethylcysteine) (XI) was found to be identical with the amino acid obtained from (VIII). The acid obtained from 3,3-dimethylcysteine and 2-bromopropionic acid was found to be widely different in its properties: it could be obtained only in the form of its hydrochloride. When an attempt was made to obtain the acid (XII) in the free state, elimination of water unexpectedly occurred with ring closure, yielding the compound (X) containing a six-membered ring:



(X)

It was thus shown that the condensation product formed by 3,3-dimethylcysteine with 3-chloropropionyl chloride contains a seven-membered ring.

Unusually facile cyclization was observed also in the alkylation of 3,3-dimethylcysteine with bromoacetic acid, the product being 2,2-dimethyl-5-oxo-3-thiamorpholinecarboxylic acid (XIV):



(XIII) (XIV)

The 2,2-dimethyl-5-oxo-3-thiamorpholinecarboxylic acid so obtained was found to be identical with the previously obtained [3] product of the condensation of 3,3-dimethylcysteine with chloroacetyl chloride. Unlike S-(carboxymethyl)-3,3-dimethylcysteine (XIII), S-(2-carboxyethyl)-3,3-dimethylcysteine (XI) does not undergo cyclization under these conditions.

EXPERIMENTAL

N-Acetyl-3,3-dimethylcysteine (I). a) Sodium acetate (7 g) was added to a solution of 10 g of the hydrobromide of 3,3-dimethylcysteine in 25 ml of water, and after 10-15 minutes the mixture was shaken vigorously while 5.0 g (20% excess) of acetic anhydride was added. Reaction occurred with evolution of heat, and a precipitate of N-acetyl-3,3-dimethylcysteine appeared already during the first hour. The reaction mixture was set aside at room temperature overnight. On the next day the precipitate was filtered off, washed twice with small amounts of water and with alcohol, and dried in an vacuum desiccator over P_2O_5. The product was 5 g (55%) of N-acetyl-3,3-dimethylcysteine, m.p. 182-183° with decomposition. After recrystallization the melting point was 186-187°. N-Acetyl-3,3-dimethylcysteine is insoluble in ether, difficultly soluble in cold water, and readily soluble in alcohol and in hot water.

$C_7H_{13}O_3NS$. Found %: N 7.32
Calculated %: N 7.32

b) The methyl ester of N-acetyl-3,3-dimethylcysteine (0.1 g) was dissolved in the equivalent amount of 2 N aqueous NaOH. The solution was heated at 50° for 30 minutes, and was then cooled and neutralized with 2 N HCl. The resulting precipitate was filtered off, washed with water, and dried in a vacuum desiccator over P_2O_5. The product was 50 mg of N-acetyl-3,3-dimethylcysteine, m.p. 182-183°. A mixture test with the substance obtained by the acetylation of 3,3-dimethylcysteine with acetic anhydride showed no depression.

Methyl ester of 3,3-dimethylcysteine. A solution of 13 g (0.1 mole) of the hydrobromide of 3,3-dimethylcysteine in ten times the amount of absolute methanol was saturated with dry hydrogen chloride and left at room temperature for 10-12 hours. The mixture was then heated for 4-5 hours in a water bath, and the alcohol was driven off at 40-50° under reduced pressure. A solution of the residue in dry chloroform was cooled to 0°, and dry ammonia was passed until the mixture was alkaline to phenolphthalein. The resulting precipitate was filtered off and washed several times with chloroform. The united chloroform washings were evaporated down under reduced pressure, and the residue was vacuum-fractionated, yielding 5 g (60%) of the methyl ester of 3,3-dimethylcysteine, b.p. 78° (1 mm). The hydrochloride of 3,3-dimethylcysteine methyl ester melts at 184-185° with decomposition. The methyl ester of 3,3-dimethylcysteine is a colorless glycerollike liquid having a pleasant odor. It is readily soluble in water, alcohol, and ether; n_D^{20} 1.4850; d_4^{20} 1.105; found MR 42.35; calculated for $C_6H_{13}O_2NS$ MR 42.65.

Methyl ester of N-acetyl-3,3-dimethylcysteine (II). a) An ether solution of acetyl chloride (0.97 g, i.e., 0.006 mole, and 10 ml of absolute ether) was added to a vigorously shaken solution of 4 g (0.012 mole) of 3,3-dimethylcysteine methyl ester in 15 ml of absolute ether. The mixture was set aside for 10-12 hours at room temperature. The hydrochloride of 3,3-dimethylcysteine methyl ester was then filtered off and carefully washed with absolute ether; the yield was 2.3 g (94.2%); m.p. 175-180°. The united ether solutions were washed successively with N HCl, sodium bicarbonate solution, and water; they were dried over magnesium sulfate. The ether was driven off under reduced pressure until crystallization began, and 2.1 g (83.6%) of the methyl ester of N-acetyl-3,3-dimethylcysteine, m.p. 80-82° (from ether), was obtained. The methyl ester of N-acetyl-3,3-dimethylcysteine is soluble in water and very soluble in alcohol, ether, and acetone. Reactions for the thiol group with $FeCl_3$ and with sodium nitroprusside were negative; reactions with iodine and with lead acetate were positive.

	Found %	C 46.77; H 7.43; N 6.86
$C_8H_{15}O_3NS$.	Calculated %	C 46.83; H 7.3; N 6.83

b) A solution of 1 g of the methyl ester of 3,3-dimethylcysteine in 3 ml of water was treated under vigorous shaking with the theoretical amount of acetic anhydride (0.62 g). After 30 minutes the solution was extracted several times with ether, and the united ether extracts were washed successively with N HCl, sodium bicarbonate solution, and water; they were dried over magnesium sulfate. The ether was driven off under reduced pressure until crystallization began, and 0.8 g of the methyl ester of N-acetyl-3,3-dimethylcysteine, m.p. 81-83° (from ether), was obtained. A mixture test with the product of the previous experiment showed no depression.

c) A solution of 1 g of N-acetyl-3,3-dimethylcysteine in 2 ml of absolute methanol was treated with an ethereal solution of diazomethane. After 30 minutes the alcohol and ether were evaporated away under reduced pressure, and the residue was dissolved in ether. The ether solution was washed successively with sodium bicarbonate solution and with water; it was dried over magnesium sulfate. After evaporation of the solution under reduced pressure, the residue was recrystallized from a small amount of ether. A substance of m.p. 80-82°, identical with that described above, was obtained.

	Found %	N 6.76
$C_8H_{15}O_3NS$.	Calculated %	N 6.83

3-Acetyl-5,5-dimethyl-2-phenyl-4-thiazolidinecarboxylic acid (IV). N-Acetyl-3,3-dimethylcysteine (1 g) was mixed with 1.1 g (100% excess) of benzaldehyde, and 2 ml of dioxane saturated with dry HCl was added. Reaction occurred with appreciable evolution of heat; the whole went into solution, but after 10-15 minutes a new precipitate formed. On the next day the precipitate was filtered off and washed with dry ether. The product was 1.17 g (80%) of 3-acetyl-5,5-dimethyl-2-phenyl-4-thiazolidinecarboxylic acid, m.p. 172-175° with decomposition (from alcohol). The substance is readily soluble in alcohol, dioxane and hot water, but almost insoluble in ether.

	Found %	C 59.07; H 6.25; N 5.09
$C_{14}H_{17}O_3NS$.	Calculated %	C 60.2; H 6.1; N 5.02

Benzoylation of 3,3-dimethylcysteine (to give (V) and (VI)). Sodium bicarbonate (1.7 g) was added to a solution of 3 g (0.02 mole) of 3,3-dimethylcysteine in 10 ml of water, and then, at 0°, 2.8 g (0.02 mole) of benzoyl chloride and 1.7 g of sodium bicarbonate were added successively. After a short time there formed a crystalline precipitate of 4-isopropylidene-2-phenyl-2-oxazolin-5-one (VI) (1.5 g), m.p. 96-97° (from alcohol). A mixture test with an authentic sample showed no melting point depression. The filtrate was acidified with N HCl to Congo red. N-Benzoyl-3,3-dimethylcysteine (V) came down as an oil, which slowly solidified. The yield of (V) was 2 g (30%); m.p. 138-140° (from benzene). For the melting point, the literature gives 135-136°.

N-Phenylacetyl-3,3-dimethylcysteine. A solution of 1.49 g (0.01 mole) of 3,3-dimethylcysteine and 2.86 g of $Na_2CO_3 \cdot 10H_2O$ in 8 ml of water was cooled to −5° and was stirred while 1.5 g (0.01 mole) of phenylacetyl

chloride was added. After two hours the temperature was brought to that of the room, 20 ml of ether was added, and the mixture was acidified to Congo Red with 2N HCl. The ether solution was separated, and the aqueous layer was extracted twice with ether. The united ether extracts were dried over magnesium sulfate and evaporated under reduced pressure until crystallization began. The product was 0.9 g (34%) of N-phenylacetyl-3,3-dimethylcysteine, m.p. 130-131°.

	Found %:	C 58.39; H 6.56; N 5.28
$C_{17}H_{17}O_3NS$.	Calculated %:	C 58.42; H 6.36; N 5.23

Methyl ester of N-(3-chloropropionyl)-3,3-dimethylcysteine. An ether solution of 1.7 g (0.01 mole) of 3-chloropropionyl chloride was added gradually at room temperature to a solution of 3.2 g (0.02 mole) of the methyl ester of 3,3-dimethylcysteine in 100 ml of absolute ether. The mixture was set aside until the next day. The precipitate of the hydrochloride of the 3,3-dimethylcysteine ester was filtered off and carefully washed on the filter with absolute ether. The united ether solutions were washed successively with 0.1 N HCl and water. They were dried over magnesium sulfate and evaporated under reduced pressure until crystallization began. The yield of the methyl ester of N-(3-chloropropionyl)-3,3-dimethylcysteine was 1.7 g (68%): m.p. 61-62°.

	Found %:	C 42.9 H 6.5; N 5.56
$C_9H_{16}O_3NSCl$.	Calculated %:	C 42.5; H 6.3; N 5.5

Hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid (VIII). The methyl ester of N-(3-chloropropionyl)-3,3-dimethylcysteine (0.25 g, i.e., 0.001 mole) was dissolved in methanol (5 ml), and 0.5 N $Ba(OH)_2$ (4 ml) was added. The mixture was set aside at room temperature until the next day, and was then acidified to Congo Red with N HCl. The precipitate was filtered off, redissolved in sodium bicarbonate solution, and again precipitated with N HCl. The yield of hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid was 0.15 g; m.p. 266-270°.

	Found %:	C 46.04; H 6.7; N 6.87
$C_8H_{13}O_3NS$.	Calculated %:	C 47.2; H 6.3; N 6.9

N-(3-Chloropropionyl)-3,3-dimethylcysteine (VII). A solution of 0.9 g of 3,3-dimethylcysteine and 1 g of sodium bicarbonate in 10 ml of water was cooled to 0°, and 0.8 g of 3-chloropropionyl chloride was added gradually. After two hours the temperature was brought to that of the room, and the mixture was filtered and acidified to Congo Red with N HCl. The precipitate was filtered off, and recrystallization from water yielded 0.6 g (50%) of N-(3-chloropropionyl)-3,3-dimethylcysteine, m.p. 155-156°. When treated with two molecular proportions of NaOH, N-(3-chloropropionyl)-3,3-dimethylcysteine yielded the compound (VIII), m.p. 269-273°, described above; there was no depression in a mixture melting point test.

Hydrolysis of hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid. Hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid (1 g) was heated for two hours under reflux with 30 ml of a mixture of equal volumes of formic acid, hydrochloric acid, and water. The solution was filtered and evaporated to dryness under reduced pressure. The residue was dissolved in 10 ml of absolute alcohol, and 1 ml of pyridine was added. The precipitate was filtered off and washed with absolute alcohol. The product was 0.4 g of S-(2-carboxyethyl)-3,3-dimethylcysteine, m.p. 181-182°.

	Found %:	C 44.02; H 6.89; S 14.8; N 6.6
$C_8H_{15}O_4NS$.	Calculated %:	C 43.4; H 6.7; S 14.5; N 6.33

S,3,3-Trimethylcysteine. A solution of 0.15 g (0.001 mole) of 3,3-dimethylcysteine in 5 ml of water was brought to pH 8 with N NaOH, 0.15 g (0.001 mole) of methyl iodide was added, and the mixture was shaken. After 30 minutes the reaction for the thiol group was negative. The solution was acidified to pH 5.8-6 with N HCl. The precipitated S,3,3-trimethylcysteine was pressed off and recrystallized from water; m.p. 253-254° (the literature gives 254-256°). The yield was almost quantitative.

S-Benzyl-3,3-dimethylcysteine. A solution of 0.3 g (0.002 mole) of 3,3-dimethylcysteine in 6 ml of water was brought to pH 9 with N NaOH, 0.25 g (0.002 mole) of benzyl chloride was added, and the mixture was shaken at 40°. After one hour the solution was cooled and acidified to pH 5.8-6 with N HCl. The precipitated S-benzyl-3,3-dimethylcysteine was pressed off and recrystallized from water; m.p. 182-183°. A mixture test with the S-benzyl-3,3-dimethylcysteine obtained by Savard's method showed no depression.

S-(2-Carboxyethyl)-3,3-dimethylcysteine (XI). 3,3-Dimethylcysteine (0.15 g, i.e., 0.001 mole) was dissolved in 3 ml of water, and 0.2 g (0.001 mole) of 3-iodopropionic acid and 3 ml of N NaOH were added. After one hour the solution was acidified to Congo Red with N HCl and evaporated down under reduced pressure. The dry residue was dissolved in absolute ethanol and the solution filtered; 0.2 ml of pyridine was added to remove HCl.

The precipitated S-(2-carboxyethyl)-3,3-dimethylcysteine was pressed off and washed with absolute alcohol. The yield was 0.17 g (84.5%); m.p. 181-183°, undepressed by admixture of S-(2-carboxyethyl)-3,3-dimethylcysteine obtained by the hydrolysis of (VIII).

2,2,6-Trimethyl-5-oxo-3-thiamorpholinecarboxylic acid (X). a) 3,3-Dimethylcysteine (0.32 g, i.e., 0.002 mole) was dissolved in 5 ml of water, and 6.6 ml of N NaOH and 0.3 g of 2-bromopropionic acid were added. After four hours the solution was acidified to Congo Red with N HCl and evaporated to dryness under reduced pressure. The residue was dissolved in absolute ethanol and the solution filtered; 0.5 ml of pyridine was added, and the mixture was set aside for twelve hours. On the next day the alcohol was evaporated off, 5 ml of water was added, and the solution was filtered. After recrystallization from water the melting point of the substance (X) was 188-189°.

	Found %:	C 46.3; H 6.7; S 15.6; N 7.11
$C_8H_{13}O_3NS$.	Calculated %:	C 47.2; H 6.4; S 15.7; N 6.9

b) The substance (X) was obtained also by the acylation of 3,3-dimethylcysteine with 2-bromopropionyl bromide by the Schotten-Baumann method.

Hydrochloride of S-(1-carboxyethyl)3,3-dimethylcysteine (XII). A mixture of 0.1 g of 2,2,6-trimethyl-5-oxo-3-thiamorpholinecarboxylic acid (X) and 2 ml of 15% HCl was heated for two hours under reflux. The solution was then evaporated to dryness under reduced pressure. The residue was dissolved in absolute alcohol, and five times the volume of absolute ether was added, when a precipitate formed of the hydrochloride of S-(1-carboxyethyl)-3,3-dimethylcysteine (XII), m.p. 172-174° with decomposition (in a closed capillary).

	Found %:	C 37.3; H 6.3; N 5.9
$C_8H_{16}O_4NSCl$.	Calculated %:	C 37.0; H 6.2; N 5.4

Methyl ester of N-(2-bromopropionyl)-3,3-dimethylcysteine. The methyl ester of 3,3-dimethylcysteine (3.2 g, i.e., 0.02 mole) was dissolved in absolute ether (150 ml), and a solution of 2,2 g (0.01 mole) of 2-bromopropionyl bromide in ether was added. The mixture was set aside at room temperature for twelve hours. The precipitated hydrobromide of the methyl ester of 3,3-dimethylcysteine was pressed off and washed with ether. The united ether solutions were washed with N HCl and with water, and were dried over magnesium sulfate. The ether was evaporated off until crystallization began. The crystals were filtered off and washed with a small amount of ether, and 1.4 g (50%) of the methyl ester of N-(2-bromopropionyl)-3,3-dimethylcysteine, m.p. 71-72°, was obtained.

	Found %:	C 36.3; H 5.41
$C_9H_{16}O_3NSBr$.	Calculated %:	C 36.2; H 5.3

S-(carboxymethyl)-3,3-dimethylcysteine (XIII). 3,3-Dimethylcysteine (0.75 g, i.e., 0.005 mole) was dissolved in 5 ml of water, and 5 ml of 2 N NaOH was added. Bromoacetic acid (0.7 g, i.e., 0.005 mole) was then added gradually. After two hours the mixture was acidified to Congo Red with N HCl and evaporated under reduced pressure. The dry residue was dissolved in absolute alcohol, and the solution was filtered; 1 ml of pyridine was added to remove HCl, and the mixture was set aside for five hours. The precipitate was filtered off and washed with absolute alcohol, and 0.3 g of S-(carboxymethyl)-3,3-dimethylcysteine, m.p. 147° with decomposition, was obtained.

	Found %:	C 39.4; H 6.05; N 6.4
$C_7H_{13}O_4NS$.	Calculated %:	C 40.5; H 6.2; N 6.7

2,2-Dimethyl-5-oxo-3-thiamorpholinecarboxylic acid (XIV). a) Pyridine (0.1 ml) was added to a solution of 0.1 g of the hydrochloride of S-(carboxymethyl)-3,3-dimethylcysteine in 4 ml of absolute alcohol. The mixture was set aside at room temperature for twelve hours. The alcohol was then evaporated off, 2 ml of water was added, and the precipitated 2,2-dimethyl-5-oxo-3-thiamorpholinecarboxylic acid was pressed off. After recrystallization from water the substance (XIV) melted at 172-173°. A mixture test with a sample prepared by a previously known method [3] showed no melting point depression.

b) S-(Carboxymethyl)-3,3-dimethylcysteine (0.2 g) was heated at 100° in a vacuum over phosphoric anhydride for three hours, and the substance (XIV), m.p. 172-173°, was obtained. Unlike the free acid, the hydrochloride of S-(carboxymethyl)-3,3-dimethylcysteine does not undergo cyclization under these conditions.

Methyl ester of N-(2,3-dibromopropionyl)-3,3-dimethylcysteine. A solution of 1.25 g (0.005 mole) of 2,3-dibromopropionyl chloride in 10 ml of absolute ether was added to a solution of 1.63 g (0.01 mole) of the methyl ester of 3,3-dimethylcysteine in 25 ml of absolute ether. The precipitated hydrochloride of the methyl ester of 3,3-dimethylcysteine was pressed off and washed with ether. The united ether solutions were washed with N HCl and with water, and were dried over magnesium sulfate. Ether was removed under reduced pressure until crystallization began, and a quantitative yield of the methyl ester of N-(2,3-dibromopropionyl)-3,3-dimethylcysteine, m.p. 92-93°, was

obtained. After recrystallization from hot water it melted at 101-102°. The substance is readily soluble in ether, alcohol, and dioxane, but difficultly soluble in petroleum ether.

	Found %:	C 29.11; H 4.1; N 4.1
$C_5H_{11}O_3NSBr_2$.	Calculated %:	C 28.64; H 3.98; N 3.71

SUMMARY

1. It has been shown that 3,3-dimethylcysteine is readily acylated by means of acid anhydrides and acid chlorides and that it then forms only N-acyl derivatives.

2. 3,3-Dimethylcysteine is readily alkylated in aqueous alkaline solution, particularly by halogen-substituted acids, with formation of only S-alkyl derivatives. With acid chlorides of β-halo carboxylic acids, 3,3-dimethylcysteine forms derivatives of hexahydro-1,4-thiazepin-5-one.

3. It has been shown that the products of the S-alkylation of 3,3-dimethylcysteine with α-bromo carboxylic acids are readily converted into derivatives of 3-thiamorpholinone, which is an unusual case of the spontaneous acylation of an amino group by a carboxylic acid.

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N. D. Zelinsky Institute of Organic Chemistry
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[3] The Chemistry of Penicillin, 1949, 938.

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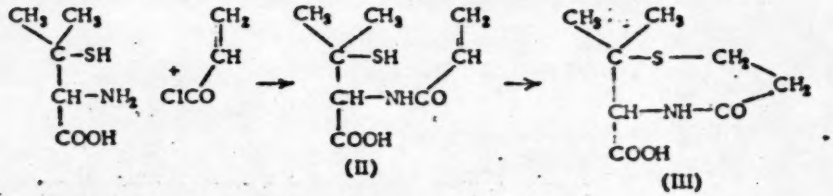
REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 3. ACYLATION AND ALKYLATION OF 3, 3-DIMETHYLCYSTEINE

I. L. Knunyants, O. V. Kildisheva, and M. G. Linkova

We have previously shown that N-(3)chloropropiony)-3,3-dimethylcysteine readily undergoes cyclization in presence of alkali with formation of hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid (I) [1]. When 3,3-dimethylcysteine is acylated with acryloyl chloride, N-acryloyl-3,3-dimethylcysteine (II) is readily formed, and in presence of alkali intramolecular reaction between the thiol group and the acryloyl residue occurs with formarion of the compound (III), identical with hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid (I):

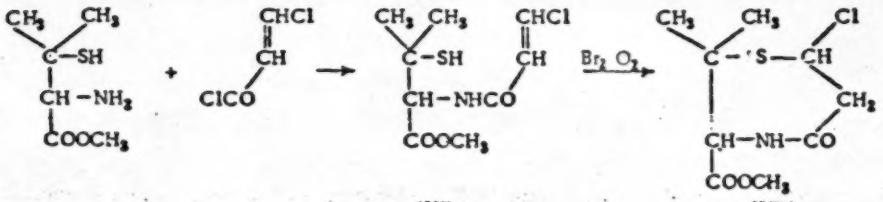


(II) (III)

When the methyl ester of 3,3-dimethylcysteine is acylated with acryloyl chloride, a quantitative yield is obtained of the methyl ester of N-acryloyl-3,3-dimethylcysteine (IV), which is again converted into a cyclic acid identical with (III) when hydrolyzed with alkali. With diazomethane, hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid (III) is converted into the corresponding methyl ester (V).

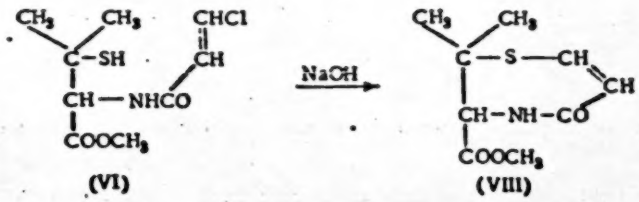
The possibility of the intramolecular addition of the thiol group of 3,3-dimethylcysteine to the double bond of the acrylic residue has thus been demonstrated.

Acylation of 3,3-dimethylcysteine methyl ester with 3-chloroacryloyl chloride yields the methyl ester of N-(3-chloroacryloyl)-3,3-dimethylcysteine (VI), which, unlike N-acryloyl-3,3-dimethylcysteine (II), cyclizes with difficulty, the product being the compound (VII):



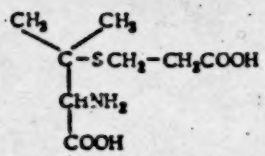
(VI) (VII)

Addition of the thiol group is not accelerated by ultraviolet radiation or by Triton B, and only in presence of benzoyl peroxide was the compound (VII) obtained in limited yield. In presence of alkali (VI) is readily converted into the unsaturated seven-membered ring compound (VIII):

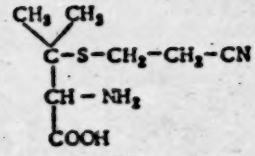


(VI) (VIII)

Addition of acrylic acid to 3,3-dimethylcysteine yields the already known S-(2-carboxyethyl)-3,3-dimethylcysteine (IX) [1]. Acrylonitrile reacts similarly with 3,3-dimethylcysteine, forming S-(2-cyanoethyl) -3,3-dimethylcysteine (X):



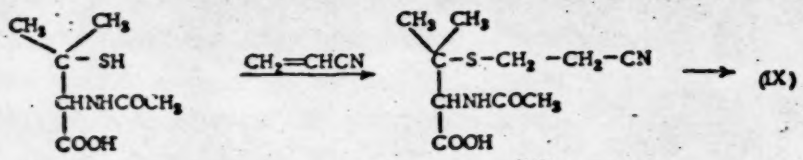
(IX)



(X)

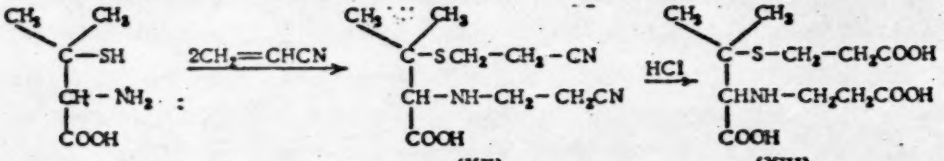
The structures of the compounds obtained, as S-derivatives of 3,3-dimethylcysteine, were proved by the following series of transformations.

Compound (X) was readily converted by hydrolysis with hydrochloric acid into the dicarboxylic acid (IX), which was found to be identical with the dicarboxylic acid obtained both by the alkylation of 3,3-dimethylcysteine with 3-iodopropionic acid and also by the scission of hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid [1]. The dicarboxylic acid was obtained also by the action of acrylonitrile on N-acetyl-3,3-dimethylcysteine, followed by hydrolysis of the addition product (XI) with hydrochloric acid:



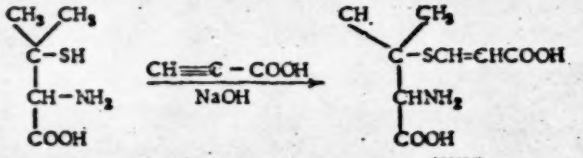
(XI)

It should be noted that acrylonitrile adds to 3,3-dimethylcysteine much more readily than acrylic acid does. In presence of an excess of acrylonitrile, the amino group of 3,3-dimethylcysteine also reacts, and the N,S-disubstituted product (XII) is obtained; this dinitrile may be hydrolyzed to the tricarboxylic acid (XIII):



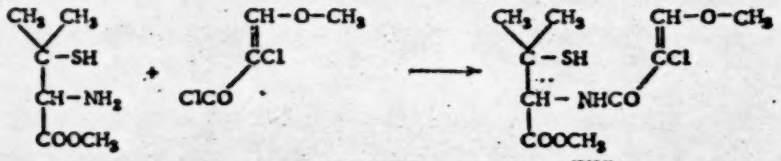
(XII) (XIII)

Dimethylcysteine readily adds to propiolic acid with formation of the dicarboxylic acid (XIV):



(XIV)

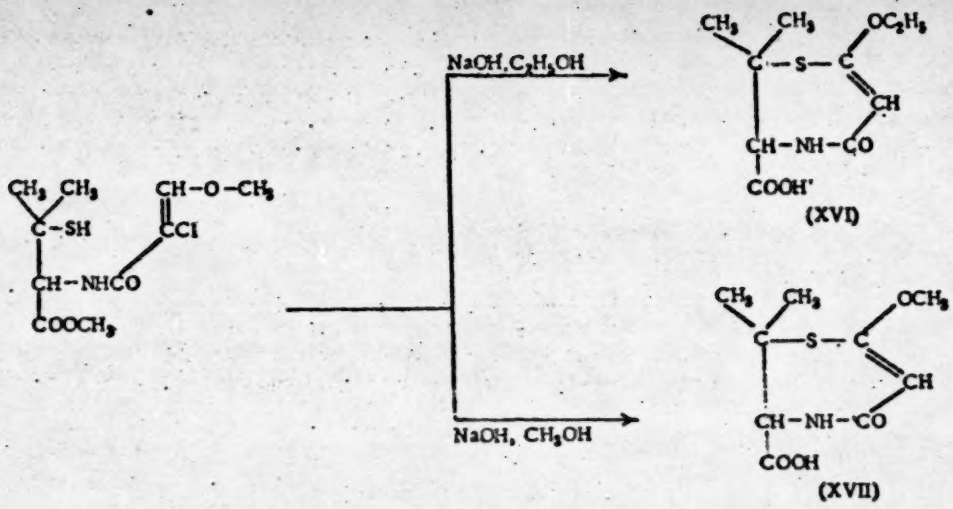
Acylation of the methyl ester of 3,3-dimethylcysteine with 2-chloro-3-methoxyacrylic acid yields the methyl ester of N-(2-chloro-3-methoxyacryloyl) -3,3-dimethylcysteine (XV):



(XV)

The presence of a free thiol group is shown by qualitative reactions with iodine and with lead acetate (yellow precipitate of mercaptide).

Hydrolysis of the ester group of (XV) with an alcoholic solution of caustic soda yields the cyclic compound (XVI) with simultaneous elimination of HCl and replacement of the alkoxy group in the ring by the residue of the alcohol in which the alkali is dissolved. Thus, when the methyl ester of N-(2-chloro-3-methoxyacryloyl)-3,3-dimethylcysteine is treated with ethanolic caustic soda, the corresponding ethoxy derivative (XVI) is obtained, and when it is treated with methanolic alkali the product is the corresponding methoxy derivative (XVII):



With diazomethane, the ethoxy derivative is readily converted into the methyl ester of 7-ethoxy-2,3,4,5-tetrahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid.

EXPERIMENTAL

N-Acryloyl-3,3-dimethylcysteine (II). Sodium bicarbonate (1.2 g) was added to a solution of 0.45 g (0.003 mole) of 3,3-dimethylcysteine in 10 ml of water, which was then cooled to 0°. The mixture was then shaken while 0.9 g (0.009 mole) of acryloyl chloride was added in portions. After two hours the temperature was raised to that of the room, and the mixture was filtered and carefully acidified to Congo Red with N HCl. The precipitated N-acryloyl-3,3-dimethylcysteine was pressed off and recrystallized from water; m.p. 143-144°.

Found %: C 47.38; H 6.6; S 15.8
$C_8H_{13}O_2NS$. Calculated %: C 47.29; H 6.4; S 15.75

The resulting N-acryloyl-3,3-dimethylcysteine was dissolved in 0.5 N NaOH, and the solution was set aside at room temperature for twelve hours. Acidification yielded the known hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid [1]; m.p. 270° with decomposition.

Methyl Ester of N-Acryloyl-3,3-dimethylcysteine (IV). A solution of 0.9 g (0.01 mole) of acryloyl chloride in 50 ml of absolute ether was added to a solution of 3.2 g (0.02 mole) of the methyl ester of 3,3-dimethylcysteine in 150 ml of absolute ether. The mixture was set aside at room temperature for twelve hours. The precipitated hydrochloride of the methyl ester of 3,3-dimethylcysteine was pressed off and washed with absolute ether. The united ether solutions were washed with N HCl and with water, and were dried over magnesium sulfate. After removal of ether, the methyl ester of N-acryloyl-3,3-dimethylcysteine was filtered off and washed with a small amount of absolute ether. The yield was 1.7 g; m.p. 70-72°.

Found %: C 49.9; H 7.0; S 14.5 N 6.44
$C_9H_{15}O_3NS$. Calculated %: C 49.8; H 6.9; S 14.7; N 6.45

Methyl Ester of Hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic Acid (V). An alcoholic solution of caustic soda (5 ml of 0.5 N) was added to 0.2 g of the methyl ester of N-acryloyl-3,3-dimethylcysteine, and the mixture was set aside for two hours. Alcohol was removed under reduced pressure, and the residue was dissolved in 5 ml of water and acidified with N HCl. The precipitate of hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid was pressed off; m.p. 176-177° with decomposition; yield 0.12 g. A mixture test with the compound (I) [1] showed no depression. The hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid was dissolved in alcohol, and an ether solution of diazomethane was added. After partial removal of solvent a precipitate formed of the methyl ester of hexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid, m.p. 230-240° with decomposition.

Found %: C 50.16; H 7.2
$C_9H_{15}O_3NS$. Calculated %: C 49.8; H 6.9

Methyl Ester of N-(3-chloroacryloyl)-3,3-dimethylcystein (VI). A solution of 1.25 g (0.01 mole) of 3-chloroacryloyl chloride in 50 ml of absolute ether was added to a solution of 3.2 g (0.02 mole) of 3,3-dimethylcysteine methyl ester in 150 ml of absolute ether. The mixture was left for 2-3 hours at room temperature. The precipitated

hydrochloride of 3,3-dimethylcysteine methyl ester was pressed off and repeatedly washed with absolute ether. The united ether solutions were washed with N HCl and with water, and were dried rapidly over magnesium sulfate. The solution was filtered and left until the next day, when a small amount of a precipitate of the methyl ester of 7-chlorohexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid had formed (m.p. 226-227°). The ether was evaporated under reduced pressure until crystallization began, and the methyl ester of N-(3-chloroacryloyl)-3,3-dimethylcysteine, m.p. 77-78°, was obtained.

	Found %:	C 43.3; H 5.6
$C_9H_{14}O_3NSCl$.	Calculated %:	C 42.9; H 5.5

Methyl Ester of 7-Chlorohexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic Acid (VII). Benzoyl peroxide (0.2 g) was added to a solution of 1 g of the methyl ester of N-(3-chloroacryloyl)-3,3-dimethylcysteine in 100 ml of ether, and the mixture was set aside at room temperature until the next day. A yield of 0.05 g of the methyl ester of 7-chlorohexahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid was obtained (m.p. 226-227°).

	Found %:	C 43.4; H 5.4
$C_9H_{14}O_3NSCl$.	Calculated %:	C 42.9; H 5.5

Methyl Ester of 2,3,4,5,-Tetrahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic Acid (VIII). The methyl ester of N-(3-chloroacryloyl)-3,3-dimethylcysteine (0.125 g) was dissolved in 100 ml of absolute ether, and an equivalent amount of methanolic N NaOH was added gradually. The mixture was stirred for two hours. Ether was removed under reduced pressure, and the residue was pressed off and washed with water. The product was 0.17 g of the methyl ester of 2,3,4,5-tetrahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid, m.p. 155-160°.

	Found %:	C 48.7; H 6.4; N 6.48
$C_9H_{13}O_3NS$.	Calculated %:	C 50.2; H 6.05; N 6.51

The aqueous mother liquor contained the theoretical amount of sodium chloride (determined by Volhard's method).

S-(2-Carboxyethyl)-3,3-dimethylcysteine (IX). a) A solution of 0.3 g (0.002 mole) of 3,3-dimethylcysteine in 4 ml of water was mixed with 0.15 g (0.002 mole) of acrylic acid, and 10% ammonia was added to pH 7. The mixture was heated in a water bath at 100° for 90 minutes, cooled, acidified to Congo Red, and evaporated under reduced pressure. The dry residue was dissolved in absolute alcohol, and 0.3 ml of pyridine was added to remove HCl. The precipitated S-(2-carboxyethyl)-3,3-dimethylcysteine was filtered off and washed with alcohol. A yield of 0.07 g was obtained of a substance of m.p. 177-179°. A mixture test with the S-(2-carboxyethyl)-3,3-dimethylcysteine obtained from 3,3-dimethylcysteine and 3-iodopropionic acid showed no depression.

b) Acrylonitrile (0.2 g) was added to a solution of 0.57 g (0.003 mole) of N-acetyl-3,3-dimethylcysteine in 3.5 ml of caustic soda solution (0.16 g of NaOH). The temperature rose spontaneously to 39°. After 30 minutes, 4.5 ml of hydrochloric acid (sp. gr 1.19) was added, and the mixture was heated for two hours under reflux. The solution was then evaporated under reduced pressure, and the dry residue was dissolved in absolute alcohol. The solution was filtered, and S-(2-carboxyethyl)-3,3-dimethylcysteine, m.p. 178-179°, was isolated as described above.

S-(2-Cyanoethyl)-3,3-dimethylcysteine (X). 3,3-Dimethylcysteine (0.45 g, i.e. 0.003 mole) was dissolved in 5 ml of water containing 0.12 g of caustic soda. The resulting alkaline solution was stirred, and 0.2 g of acrylonitrile was gradually added at 25-26° over a period of one hour. The solution was acidified with 80% acetic acid and diluted with twice its volume of ethanol. The precipitated S-(2-cyanoethyl)-3,3-dimethylcysteine was filtered off and recrystallized from 50% alcohol. The product was 0.5 g of the substance (X), m.p. 181-182°.

	Found %:	S 15.3; N 13.65
$C_8H_{14}O_2N_2S$.	Calculated %:	S 15.8; N 13.86

N,S-Bis(2-cyanoethyl)-3,3-dimethylcysteine (XII). 3,3-Dimethylcysteine (0.6 g, i.e. 0.004 mole) was dissolved in caustic soda solution (containing 0.16 g of NaOH), and 0.3 g (0.008 mole) of acrylonitrile was added. The temperature rose spontaneously to 32°. After 30 minutes the solution was acidified with 80% acetic acid and diluted with five times its volume of ethanol. The precipitated N,S-bis(2-cyanoethyl)-3,3-dimethylcysteine was filtered off and washed with alcohol. The product was 0.5 g of the substance (XII), m.p. 149-150°.

	Found %:	C 51.9; H 6.9; S 12.5; N 16.4
$C_{11}H_{17}O_2N_3S$.	Calculated %:	C 51.8; H 6.66; S 12.5; N 16.4

N,S-Bis(2-carboxyethyl)-3,3-dimethylcysteine (XIII). A mixture of 0.5 g of N,S-bis(2-cyanoethyl)-3,3-dimethylcysteine and 10 ml of 15% HCl was heated under reflux for five hours and then evaporated under reduced pressure. The dry residue was dissolved in absolute alcohol, and the solution was filtered. Addition of 0.5 ml of pyridine precipitated N,S-bis(2-carboxyethyl)-3,3-dimethylcysteine m.p. 187-188°, in quantitative yield.

Found %: C 45.07; H 6.58; S10.56; N 4.89

$C_{11}H_{13}O_6NS$. Calculated %: C 45.05; H 6.51 S10.92; N 4.77

S-(2-Carboxyvinyl)-3,3-dimethylcysteine (XIV). Propiolic acid (0.2 g, i.e. 0.003 mole) was added to a solution of 0.45 g (0.003 mole) of 3,3-dimethylcysteine in 7 ml of N NaOH. The mixture was set aside for 3-4 hours at room temperature, acidified to Congo Red with N HCl, and evaporated to dryness. The residue was dissolved in absolute alcohol, and the solution filtered. Pyridine (0.5 ml) was then added, and the solution was set aside at room temperature for twelve hours. The product was 0.2 g of S-(2-carboxyvinyl)-3,3-dimethylcysteine, m.p. 153-154°.

Found %: S 14.6; N 6.47

$C_8H_{13}O_4NS$. Calculated %: S 14.6; N 6.35

Methyl Ester of N-(2-Chloro-3-methoxyacryloyl)-3,3-dimethylcysteine (XV). A solution of 8 g of 2-chloro-3-methoxyacrylic acid in 100 ml of absolute ether was added to a solution of 17 g of the methyl ester of 3,3-dimethylcysteine in 250 ml of absolute ether, and the mixture was set aside at room temperature for twelve hours. On the next day the hydrochloride of the methyl ester of 3,3-dimethylcysteine was pressed off and carefully washed with absolute ether. The united ether solutions were washed with N HCl and with water, and were dried over magnesium sulfate. Ether was removed under reduced pressure until crystallization began. The yield of the methyl ester of N-(2-chloro-3-methoxyacryloyl)-3,3-dimethylcysteine was 12.6 g (86%). After recrystallization from ether it melted at 64-66°. The substance is readily soluble in alcohol and ether, but insoluble in water.

Found %: C 42.67; H 5.86; S 11.23; Cl 12.5; N 5.1

$C_{10}H_{16}O_4NSCl$. Calculated %: C 42.7; H 5.7; S 11.3; Cl 12.6; N 4.97

7-Ethoxy-2,3,4,5,-tetrahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic Acid (XVI). The methyl ester of N-(2-chloro-3-methoxyacryloyl)-3,3-dimethylcysteine (2.8 g, i.e. 0.01 mole) was dissolved in 12 ml of 2 N ethanolic NaOH, and the solution was set aside at room temperature for twelve hours. Absolute ether (20 ml) was then added, and the precipitate that formed was filtered off, dissolved in the least possible amount of water, and acidified with 2 N HCl until precipitation was complete. The precipitate of 7-ethoxy-2,3,4,5-tetrahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid was filtered off and washed with water. After recrystallization from alcohol the substance (XVI) melted at 187-188°. The yield was 0.9 g (40.5 %).

Found %: C 48.5; H 6.17; S 12.78; N 5.88; OC_2H_5 18.07

$C_{10}H_{16}O_4NS$. Calculated %: C 48.8; H 6.12; S 13.06; N 5.68 OC_2H_5 18.3

2,3,4,5 -Tetrahydro-7-methoxy-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic Acid (XVII). The methyl ester of N-(2-chloro-3-methoxyacryloyl)-3,3-dimethylcysteine (1.4 g, i.e. 0.005 mole) was dissolved in 7 ml of 2 N methanolic NaOH, and the solution was set aside at room temperature for twelve hours. Absolute ether (10 ml) was added, and the resulting precipitate was filtered off, dissolved in the least possible amount of water, and acidified with 2 N HCl until precipitation was complete. The precipitate of 2,3,4,5-tetrahydro-7-methoxy-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic acid was pressed off and washed with water. After recrystallization from 50% alcohol the substance (XVII) melted at 216-219°. The yield was 0.7 g (60.5%).

Found %: C 46.52; H 5.66; N 6.05

$C_9H_{14}O_4NS$. Calculated %: C 46.55; H 5.63; N 6.0

Methyl Ester of 7-Ethoxy-2,3,4,5-tetrahydro-2,2-dimethyl-5-oxo-1,4-thiazepine-3-carboxylic Acid (XVIII). A solution of 0.5 g of the substance (XVI) in 1 ml of methanol was treated with an ether solution of diazomethane until nitrogen ceased to be evolved. Alcohol and ether were removed under reduced pressure until crystallization began. The precipitate was filtered off and recrystallized from ether. The product was 0.3 g (58%) of the substance (XVIII), m.p. 86-88°. The substance is very readily soluble in alcohol and ether.

Found %: C 50.82; H 6.67; N 5.46

$C_{11}H_{17}O_4NS$ Calculated %: C 50.96; H 6.56; N 5.4

SUMMARY

1. A number of substituted N-acryloyl derivatives of 3,3-dimethylcysteine, having bromine, chlorine, and methoxyl in the acyl residue, have been prepared.

2. It has been shown that these derivatives undergo cyclization by the intramolecular addition of the thiol group of the dimethylcysteine to the double bond of the acryloyl residue with formation of hexahydro-1,4-thiazepin-5-ones.

3. It has been shown that, in the reaction of 3,3-dimethylcysteine with unsaturated acids and their derivatives, the main process occurring is the addition of the thiol group of the dimethylcysteine to the double bond with formation of S-carboxyalkyl derivatives of 3,3-dimethylcysteine.

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M. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

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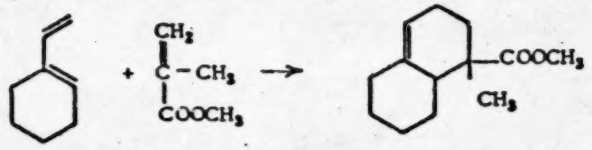
* Consultants Bureau Translation, this issue, p. 53.

STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 4. CONDENSATION OF 1-VINYLCYCLOHEXENE WITH CITRACONIC ANHYDRIDE

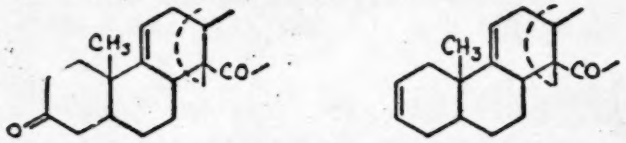
I. N. Nazarov, V. F. Kucherov, and V. M. Andreev

A study of the condensation of 1-vinylcyclohexene with such dienophiles as acrolein, methacrylic acid, and methyl methacrylate [1] has shown that in this reaction predominant formation of the ortho isomer occurs:



The dimerization of 1-vinylcyclohexene [2] and its condensation with 2-cyclohexen-1-one [3] also proceed according to this ortho-condensation scheme. The condensation of 1-vinylcyclohexene with 2,4-dimethyl-2-cyclopenten-1-one [4] is more complex, but in this case also, the reaction products have the structure of ortho adducts.

Studies by Nazarov and coworkers [5] have shown that, when various bicyclic vinylcycloalkenes condense with α,β-unsaturated cyclic ketones, the product is a mixture of stereoisomeric tetracyclic ketones of ortho structure (the so-called "inverted" steroid structure).



In those diene condensations in which the bicyclic diene has one aromatic ring, a mixture of the two possible ortho and meta adducts is formed, as was shown in the case of the condensation of 1,2-dihydro-7-methoxy-4-vinylnaphthalene with citraconic anhydride [6] and with 2-cyclopenten-1-one [7].

In such condensations, the course of the reaction presents great interest not only in relation to structural questions, but also with respect to questions of stereochemistry, which, as is well known, are of very great importance in the synthesis of polycyclic compounds related to the steroids. With a view to the further systematic study of the structural and spatial aspects of the course of the diene synthesis, we have made a detailed investigation of the condensation of 1-vinylcyclohexene (I) with citraconic anhydride (II). We have found that prolonged heating (11-15 hours) of the mixture of reactants (40% excess of diene) at 100° gave a 92% yield of a mixture of crystalline and liquid anhydrides (III) and (IV). Hydrolysis of this mixture with 3% aqueous caustic soda resulted in the isolation of two isomeric crystalline cis acids (V) and (VI) in the ratio of 5 : 1 approximately. The structures of these acids were proved by dehydrogenation in presence of palladized charcoal (10% Pd) at 360-370° for 18 hours. The cis acid (V) then yielded 1-methylnaphthalene, identified as the picrate, m.p. 138.5-140°, undepressed by admixture with an authentic sample. The acid (VI), when dehydrogenated under the same conditions, yielded 2-methylnaphthalene, characterized as the picrate, m.p. 114-114.5°, also undepressed by admixture with an authentic sample.

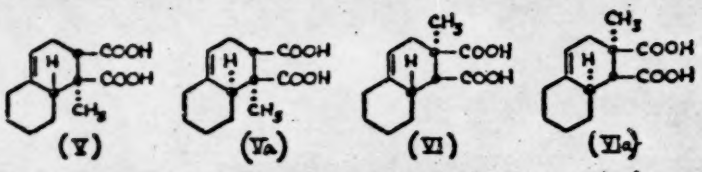
These results show that the cis acids (V) and (VI) are structural isomers, and that in the present case the two possible structures, ortho and meta, are formed, with considerable predominance of the ortho isomer (V).

No other products were isolated in the condensation of 1-vinylcyclohexene with citraconic anhydride at 100°. At a lower temperature (20°) the reaction is slower, and under these conditions only the cis anhydride (III) was isolated. After condensation at a high temperature (220-230°) and subsequent hydrolysis, the acids (V) and (VI) were again isolated in about the same proportions (5:1). The cis anhydride (III) is thermally stable, being practically unchanged by heating at 200° for two hours.

The cis structure of the acids (V) and (VI) follows from the method of preparation, and the readiness with which the double bond undergoes hydrogenation and its displacement in presence of a mixture of hydrochloric and

acetic acids (see below) indicate that it occurs in the normal position (the 4-position).

In accordance with the method of synthesis (the cis principle of the diene condensation), each of the cis acids (V) and (VI), with their three asymmetric carbon atoms (bold points in the formulas), can exist in the form of two stereoisomers:



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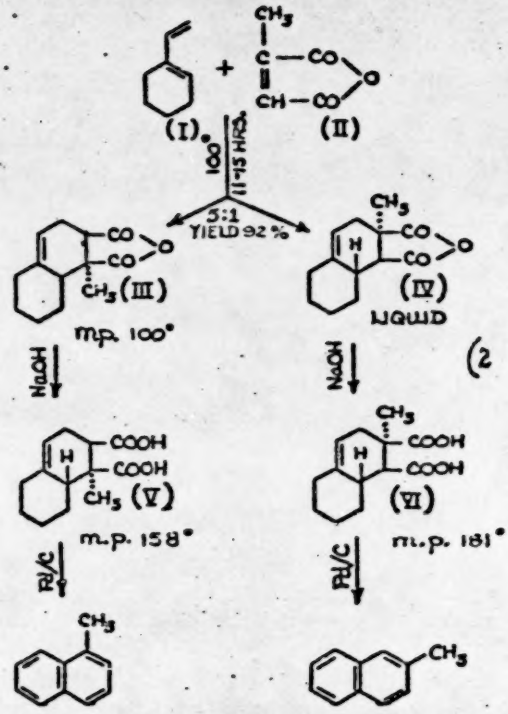
The fact that only one isomer is formed for each structural species indicates that, under our conditions, quite definite steric orientation occurs in the diene synthesis. The thermal stability of the adducts obtained gives us reason to suppose (in accord with Stuart atomic models) that these adducts have spatial configurations corresponding to the formulas (V) and (VI); their formation occurs by "exo-addition" with violation of the principle of "maximum accumulation of unsaturation", a phenomenon that has been observed several times before in diene condensations at high temperatures [8].

A number of the reactions of the cis acids (V) and (VI) were studied, and these enabled us to examine their structures in greater detail. When cis-1,2,3,5,6,8,8a-octahydro-1-methyl-1,2-naphthalenedicarboxylic acid (V) and its anhydride (III) were hydrogenated in presence of a platinum catalyst, addition of one molecule of hydrogen readily occurred with formation of the pure substances (VIII) and (VII) respectively, the spatial configurations of which follow from the cis principle of hydrogenation. Treatment of the cis acids (V) and (VIII) with acetyl chloride yielded the cis anhydrides (III) and (VII), and treatment with diazomethane yielded the corresponding cis diesters (IX) and (X); the latter was readily obtained also by hydrogenation of the unsaturated cis diester (IX) in presence of a platinum catalyst.



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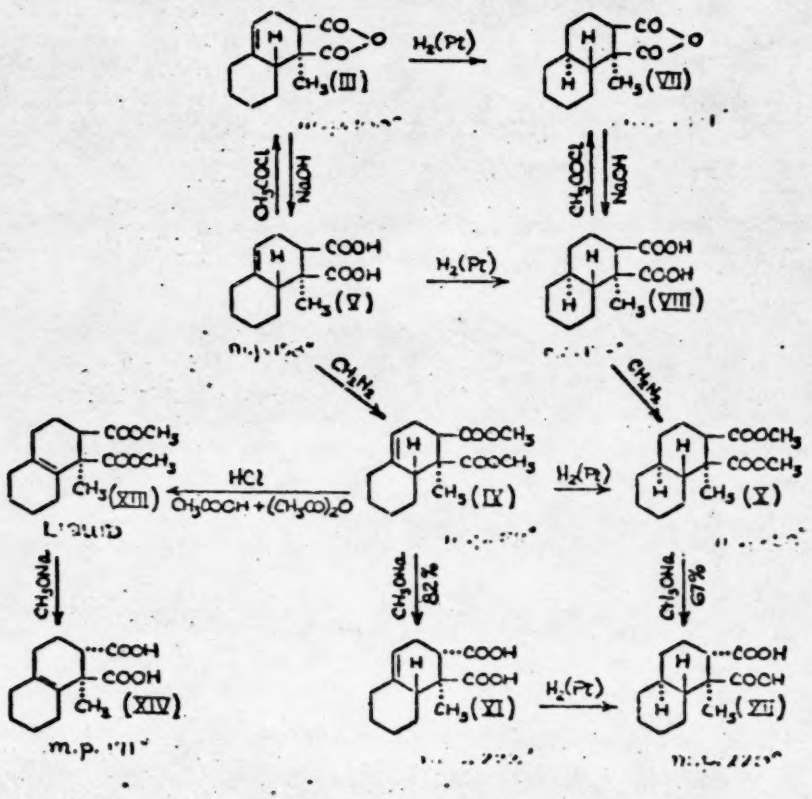
Thus, the hydrogenation of the cis anhydride (III), acid (V), and ester (IX) is sterically selective, which is to be explained by the screening effect of the cis substituents at C-1, C-2, and C-8a (see below), as a result of which the hydrogen adds at the double bond at the side opposite to these substituents (the less screened side).

By isomerization of the cis diesters (IX) and (X) in presence of sodium methoxide, good yields were readily obtained of the corresponding trans-1,2,3,5,6,7,8,8a-octahydro-1-methyl-1,2-naphthalenedicarboxylic acid (XI), m.p. 222°, and trans-decahydro-1-methyl-1,2-naphthalenedicarboxylic acid (XII), m.p. 229°.

The crystalline cis diester (IX), when treated at 60° with a mixture of acetic anhydride and acetic acid saturated with dry hydrogen chloride, isomerized into the liquid diester (XIII) with displacement of the double bond, and this, when isomerized in presence of sodium methoxide, yielded the new trans acid (XIV), m.p. 170-171°. Unlike the compounds (IX) and (XI), the cis diester (XIII) and the trans acid (XIV) showed little tendency to undergo hydrogenation in presence of a platinum catalyst under the usual conditions, a fact that confirms the inter-ring position of the double bond.

The above-described reactions were carried out also for the case of the isomeric cis-1,2,3,5,6,7,8,8a-octahydro-2-methyl-1,2-naphthalenedicarboxylic acid (VI). The unsaturated cis anhydride (IV) and the corresponding acid (VI) were readily hydrogenated in presence of a platinum catalyst with formation of the pure individual anhydride

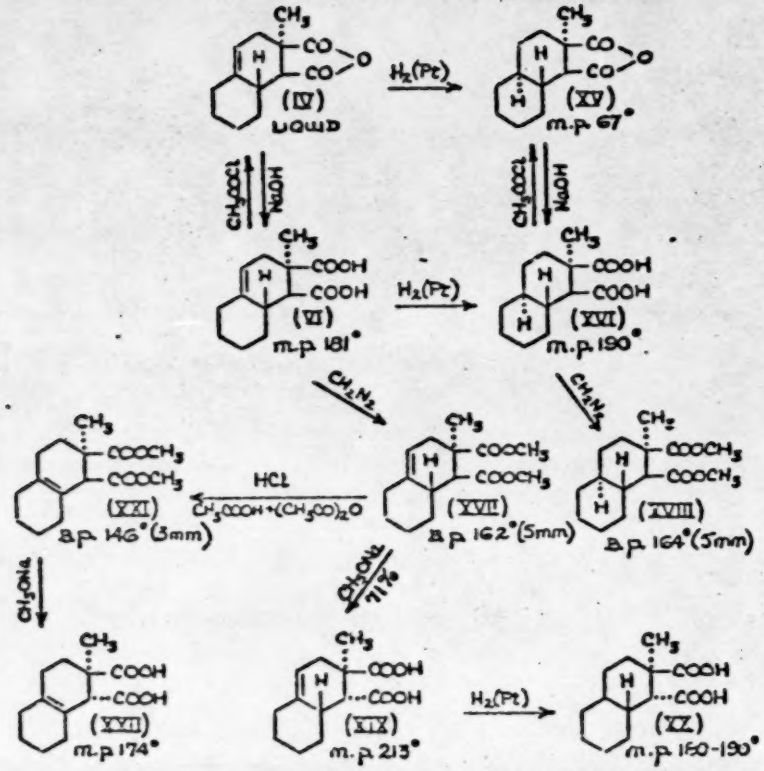
(XV) and acid (XVI). In this case again, therefore, the hydrogenation of the cis anhydride (IV) and the cis acid (VI) proceed in a selective manner, which is to be explained by the same steric factors as in the case of the hydrogenation of the cis compounds (III), (V), and (IX).



Treatment of the cis acids (VI) and (XVI) with diazomethane yielded the corresponding cis diesters (XVII) and (XVIII). Isomerization of the cis diester (XVII) in presence of sodium methoxide gave a good yield of trans-1,2,3,5,6,7,8,8a-octahydro-2-methyl-1,2-naphthalenedicarboxylic acid (XIX), m.p. 213°. The hydrogenation of this trans acid in presence of a platinum catalyst is now no longer selective, and a mixture of isomeric saturated acids (XX), m.p. 180-190°, was obtained attempts to separate these by crystallization were not successful. It must be pointed out that the catalytic hydrogenation at platinum of the trans acid (XI), unlike that of the trans acid (XIX), proceeds in a sterically selective manner. This interesting fact indicates that in such compounds the screening of the double bond is effected by cis substituents at (C-1) — (C-8a), and not by substituents at (C-1) — (C-2). When there is a trans disposition of substituents at (C-1) — (C-8a), as in the trans acid (XIX) (see Communication 5), sterically oriented hydrogenation becomes impossible. This conclusion is confirmed also by an examination of Stuart atomic models.

When treated with a mixture of acetic anhydride and acetic acid saturated with hydrogen chloride, the cis diester (XVII) yields the new liquid diester (XXI), which isomerizes in presence of sodium methoxide into the trans acid (XXII), m.p. 174°. The cis diester (XXI) and the trans acid (XXII), in which the double bond is in the inter-ring position, are not hydrogenated at a platinum catalyst under normal conditions.

All of these transformations of the isomeric acids (V) and (VI) show that they are cis-1,2,3,5,6,7,8,8a-octahydro-1- and -2-methyl-1,2-naphthalenedicarboxylic acids having the spatial configuration corresponding to the more stable structure formed by "exo-addition".



EXPERIMENTAL

Condensation of 1-Vinylcyclohexene with Citraconic Anhydride

A mixture of 50 g of 1-vinylcyclohexene (I) [9], 36 g of citraconic anhydride [10], and a little (about 0.2 g) of pyrogalloi was heated in a boiling water bath for eleven hours and then set aside at room temperature for one day The precipitated crystalline product was carefully pressed off on the filter and washed with petroleum ether, and 30.7 g of a substance of m.p. 92-96° was obtained. The liquid residue obtained after removal of petroleum ether was heated in a boiling water bath for a further four hours, and was then set aside at 0° for two days. A further 3.6 g of a crystalline product, m.p. 77-89°, separated. The liquid residue remaining after removal of excess of 1-vinylcyclohexene and a small amount of citraconic anhydride by distillation was then vacuum-distilled, and yielded 22 g of a light-yellow viscous oil, b.p. 157-159°(4 mm), n_D^{20} 1.5130. From this oil, after being dissolved in an equal volume of petroleum ether and then allowed to stand at 0° overnight, a further 5.3 g of crystals, m.p. 75-84°, separated. The total yield of crystalline reaction product was 39.6 g. After recrystallization from a mixture of absolute ether and petroleum ether, 34.7 g of the pure cis anhydride (III) was obtained in long coarse needles, m.p. 99-100°

	Found %:	C 71.02; 71.18; H 7.36; 7.39
$C_{13}H_{16}O_3$	Calculated %:	C 70.92; H 7.28

The liquid reaction product was repeatedly distilled and yielded 15.7 g of the liquid cis anhydride (IV), b.p. 140-142.5°(2 mm), n_D^{18} 1.5138.

	Found %:	C 71.39; 71.29; H 7.60; 7.50
$C_{13}H_{16}O_3$	Calculated %:	C 70.92; H 7.28

The analysis of the cis anhydride (IV) showed somewhat high carbon and hydrogen contents, which may be explained by contamination with a little of the dimer of 1-vinylcyclohexene, which we did not succeed in removing by distillation.

The overall yield of condensation products was about 92% on the amount of citraconic anhydride that reacted.

cis-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (V)

A mixture of 18 g of the crystalline cis anhydride (III), m.p. 99-100°, and 250 ml of 3% aqueous caustic soda was stirred at 60° until solution was complete (90 minutes). The resulting solution was acidified to Congo Red with 1 : 1 hydrochloric acid, cooling being applied. The oil that at first separated rapidly crystallized as the mixture was stirred, and 18.5 g of a crystalline substance, m.p. 152-157°, was obtained. Recrystallization from a mixture of benzene and petroleum ether yielded 17.1 g of the cis acid (V), m.p. 157-158° with decomposition.

	Found %:	C 65.30; 65.60; H 7.62; 7.58
$C_{13}H_{18}O_4$	Calculated %:	C 65.52; H 7.53

When the cis acid (V) was boiled with acetyl chloride, the original cis anhydride (III), m.p. 98-99°, was obtained.

cis-1,2,3,5,6,7,8,8a-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (VI)

A mixture of 15.7 g of the liquid cis anhydride (IV) and 200 ml of 3% aqueous caustic soda was stirred at 60° until solution was complete (90 minutes). The dark-brown solution was treated with active charcoal and filtered, and was then acidified to Congo Red with hydrochloric acid. On standing, the thick oil that separated partially solidified. The crystalline product was carefully pressed off on the filter, and the oily contamination was washed out with a 1 : 1 mixture of acetone and petroleum ether. The product was 6.8 g of a crystalline substance, m.p. 168-172°. Two recrystallizations from a 2 : 1 mixture of benzene and acetone yielded 5 g of the cis acid (VI), having a constant melting point of 181-181.5° with decomposition.

	Found %:	C 65.55; 65.62; H 7.74; 7.70
$C_{13}H_{18}O_4$	Calculated %:	C 65.52 H 7.53

Conversion of the Cis Acid (VI) into the Anhydride (IV)

A mixture of 0.55 g of the cis acid (VI) (m.p. 180-181°) and 5.5 ml of acetyl chloride was boiled for one hour. Acetyl chloride was distilled off, and the residue was vacuum-distilled, yielding 0.4 g of the cis anhydride (IV), b.p. 157.5-158.5° (4 mm), n_D^{22} 1.5126.

Dehydrogenation of the Cis Acid (V)

A mixture of 5 g of the cis acid (V), m.p. 157-158°, 30 ml of cryoscopic benzene, and 1 g of palladized charcoal (10% Pd) was heated in an autoclave in an atmosphere of nitrogen for 18 hours at 360-370°. The mixture was filtered, the benzene was driven off, and the residue was vacuum-distilled. The product (1.3 g, b.p. 115-117° 19 mm) was again distilled under atmospheric pressure, and 0.6 g of a hydrocarbon, b.p. 237-238°, n_D^{21} 1.6080, was obtained.

In order to prepare the picrate, a solution of 0.5 g of the hydrocarbon in 2 ml of absolute ethanol was added to a warm solution of 0.81 g of picric acid in 8 ml of absolute ethanol. The voluminous precipitate of picrate was filtered off and recrystallized from ethanol; it then melted at 138.5-140°, undepressed by admixture with an authentic sample of 1-methylnaphthalene picrate (m.p. 139.5-141°). For 1-methylnaphthalene the literature [11] gives b.p. 241°, and m.p. of picrate 141-142°.

Dehydrogenation of the Cis Acid (VI)

From 1.2 g of the cis acid (VI), m.p. 181.5°, the above procedure yielded 0.6 g of a hydrocarbon, b.p. 234-240° and n_D^{22} 1.6010. The picrate melted at 114-115° and showed no depression when mixed with an authentic

sample of 2-methylnaphthalene picrate (m.p. 115-116°).

cis-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (VIII)

The cis acid (V) (2g; m.p. 157-158°) was dissolved in glacial acetic acid (25 ml) and hydrogenated over platinum oxide, when 236 ml (21°, 750 mm) of hydrogen was absorbed (one double bond required 230 ml). Acetic acid was distilled off under reduced pressure, and the crystalline residue was dissolved with the aid of heat in 20 ml of 30% aqueous caustic soda. The solution was filtered and acidified with dilute hydrochloric acid. The precipitated oil rapidly crystallized, and recrystallization from acetone yielded 1.5 g of the saturated cis acid (VIII), m.p. 177.5-178.5° with decomposition.

	Found %:	C 64.79; 65.00; H 8.30; 8.23
$C_{13}H_{22}O_4$.	Calculated %:	C 65.01; H 8.33

Anhydride of cis-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (VII)

The unsaturated cis anhydride (III) (700 mg) was dissolved in acetic acid (10 ml) and hydrogenated over platinum oxide, when one molecular proportion (83 ml) of hydrogen was absorbed. The catalyst was filtered off, and the solvent was driven off under reduced pressure; the crystalline residue was washed on the filter with petroleum ether. The product was 620 mg of the saturated cis anhydride (VII), m.p. 127-129°, which, after crystallization from petroleum ether, melted at 130-131°.

	Found %:	C 70.34; 70.12; H 8.07; 7.92
$C_{13}H_{18}O_3$.	Calculated %:	C 70.21 H 8.15

Hydrolysis of the saturated cis anhydride (VII) with 3% caustic soda gave a quantitative yield of the saturated cis acid (VIII), m.p. 177-178°; and this, when boiled with acetyl chloride, gave the cis anhydride (VII), m.p. 130-131°, in good yield.

Dimethyl Ester of cis-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (IX)

An excess of an ether solution of diazomethane was added slowly to a cooled suspension of 6 g of the cis acid (V) (m.p. 157-158°) in 100 ml of ether. The ether was distilled off, and the crystalline residue was washed on the filter with a mixture of diethyl ether and petroleum ether (1 : 7). The product was 6.2 g of the cis diester (IX), m.p. 65-67°, and this, after crystallization from a small amount of ether, had a constant melting point of 68-69°.

	Found %:	C 67.95; 67.85; H 8.51; 8.38
$C_{15}H_{22}O_4$.	Calculated %:	C 67.69; H 8.33

Dimethyl Ester of cis-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (X)

The saturated cis acid (VIII) (2.8 g) was treated as described above with an ether solution of diazomethane. The ether was driven off, and the liquid reaction product was vacuum-distilled, when 2.6 g of a viscous liquid, b.p. 165-167° (5 mm) and n_D^{20} 1.4908, was obtained. On standing, this slowly crystallized, and recrystallization from a small amount of petroleum ether yielded the crystalline cis diester (X), m.p. 49-50.5°.

	Found %:	C 67.03; 67.24; H 8.94; 9.16
$C_{15}H_{24}O_4$.	Calculated %:	C 67.16; H 9.01

The same saturated cis diester (X) may be prepared by hydrogenation of the cis diester (IX) over platinum oxide in acetic acid.

trans-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XI)

The cis diester (IX) (2.5 g) was added to a solution of 4.3 g of sodium in 160 ml of absolute methanol, and the mixture was boiled under reflux for 15 hours. Methanol distilled off until the bulk had been reduced to one-quarter, 50 ml of water was added, and the solution was boiled for a further three hours. The solution was evaporated to dryness under reduced pressure, and the residue was dissolved in the least possible amount of water and acidified with hydrochloric acid. An oil separated and gradually solidified, yielding 2.0 g of a crystalline substance, m.p. 195-207°. Recrystallization from 70% aqueous methanol yielded 1.8 g of the pure trans acid (XI), m.p. 221-222° with decomposition. The yield was 82%.

Found %: C 65.40; 65.53; H 7.63; 7.50

$C_{13}H_{18}O_4$. Calculated %: C 65.52; H 7.53

trans-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XII)

1. The cis diester (X) (2.6 g) was added to a solution of sodium methoxide prepared from 4.5 g of sodium and 150 ml of methanol, and the mixture was boiled for 15 hours. After the above-described treatment, 1.9 g of a crystalline substance, m.p. 210-225°, was isolated, and this, when crystallized from 50% aqueous acetone, yielded 1.6 g (67%) of the pure trans acid (XII) in the form of fine needles, m.p. 228-229° with decomposition.

Found %: C 64.81; 64.85; H 8.49; 8.40

$C_{13}H_{20}O_4$. Calculated %: C 65.01 H 8.33

2. The unsaturated trans acid (XI) (470 mg) was dissolved in methanol (10 ml) and hydrogenated in presence of platinum oxide and chloroplatinic acid, one molecular proportion of hydrogen (55 ml, 26°, 743 mm) being absorbed. The catalyst was filtered off, and the solvent removed under reduced pressure. The product was 400 mg of an acid of m.p. 199-204°. Two crystallizations from 50% aqueous acetone yielded the trans acid (XII) of m.p. 228-229°, undepressed by admixture of the above-described sample.

Dimethyl Ester of cis-1,2,3,4,5,6,7,8-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XIII)

The dimethyl ester of cis-1,2,3,5,6,7,8,8a-octahydro-1-methyl-1,2-naphthalenedicarboxylic acid (IX) (2.4 g; m.p. 69°) was added to 20 ml of a mixture of two parts of acetic anhydride and one part of glacial acetic acid saturated at 20° with dry hydrogen chloride, and the solution was heated at 60° for one hour. The solvents were removed under reduced pressure, and distillation of the liquid reaction product yielded 1.6 g of the cis diester (XIII), b.p. 153-154° (5 mm), n_D^{19} 1.4985.

Found %: C 67.79; 67.60; H 8.33; 8.45

$C_{15}H_{22}O_4$. Calculated %: C 67.69; H 8.33

trans-1,2,3,4,5,6,7,8-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XIV)

The cis diester (XIII) (2.0 g) was added to a solution of 5 g of sodium in 150 ml of absolute methanol, and the mixture was boiled for 15 hours. The methanol was driven off under reduced pressure, and the residue was dissolved in water (40 ml) and boiled for a further five hours. The solution was treated with charcoal and filtered; it was then evaporated to a thick slurry in a porcelain dish on a water bath. The crystalline product was filtered off and dissolved in 10 ml of water. The solution was acidified with hydrochloric acid, and the precipitated oil rapidly solidified as the mixture was stirred. The product was 1.4 g of a substance melting at 145-152°. Two recrystallizations from 40% aqueous methanol yielded the trans acid (XIV), which had a constant melting point of 170-171°.

Found %: C 65.55; 65.55; H 7.65; 7.50

$C_{13}H_{18}O_4$. Calculated %: C 65.52; H 7.53

Found: M 236.4 (by titration with NaOH)

Calculated: M 238.3

The trans acid (XIV) gave a positive reaction with tetranitromethane and was not hydrogenated in presence of platinum oxide under the usual conditions.

cis-Decahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XVI)

The cis acid (VI) (200 mg) was dissolved in glacial acetic acid (5 ml) and hydrogenated in presence of platinum oxide, one molecular proportion of hydrogen (22 ml, 21°, 750 mm) being absorbed. The catalyst was filtered off, and the acetic acid was distilled off under reduced pressure. The thick liquid residue crystallized when treated with benzene. Crystallization from a mixture of benzene and petroleum ether yielded 120 mg of the pure cis acid (XVI), m.p. 189-190° with decomposition.

Found %: C 65.19; 65.29; H 8.46; 8.56

$C_{13}H_{20}O_4$ Calculated %: C 65.01; H 8.33

Anhydride of cis-Decahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XV)

1. The cis acid (XVI) (120 mg) was boiled for 90 minutes with 1.5 ml of acetyl chloride. After removal of acetyl chloride under reduced pressure, volatile impurities were removed by distillation first with benzene and then with petroleum ether under reduced pressure; after this treatment the originally liquid residue solidified. The product was 100 mg of the crystalline saturated cis anhydride (XV), which, after crystallization from petroleum

ether, had a constant melting point of 66-67°.

	Found %:	C 70.15; 70.12; H 8.12; 8.03
$C_{13}H_{18}O_3$	Calculated %:	C 70.20; H 8.15

2. Hydrogenation of 300 mg of the liquid unsaturated cis anhydride (IV) in acetic acid over platinum oxide yielded 240 mg of a crystalline substance, m.p. 63-66°, which, after crystallization from petroleum ether, yielded the pure cis anhydride (XV) of m.p. 66-67°, identical with the product obtained in the previous experiment.

Dimethyl Ester of cis-1,2,3,5,6,7,8,8a-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XVII)

A suspension of 1.0 g of the cis acid (VI) in ether was treated with an excess of an ether solution of diazomethane. The liquid reaction product remaining after removal of ether was vacuum-distilled, and yielded 800 mg of the cis diester (XVII) in the form of a thick colorless oil, which did not crystallize when allowed to stand; b.p. 162-163° (5 mm), n_D^{18} 1.4955.

	Found %:	C 67.69; 67.70; H 8.47; 8.53
$C_{15}H_{22}O_4$	Calculated %:	C 67.69; H 8.33

Dimethyl Ester of cis-Decahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XVIII)

The cis acid (XVI) (1.7 g) was treated according to the procedure of the previous experiment with an ether solution of diazomethane, and vacuum distillation yielded 1.5 g of the cis diester (XVIII) in the form of a noncrystallizing viscous oil, b.p. 163-164° (5 mm), n_D^{15} 1.4890.

	Found %:	C 67.46; 67.50; H 8.98; 8.92
$C_{15}H_{24}O_4$	Calculated %:	C 67.17; H 9.01

trans-1,2,3,5,6,7,8,8a-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XIX)

The cis diester (XVII) (700 mg) was added to a solution of 2 g of sodium in 60 ml of absolute methanol, and the mixture was boiled for 17 hours. The methanol was distilled off under reduced pressure, and 15 ml of water was added to the residue. The solution was then boiled for five hours, after which it was evaporated down to a thick slurry in a porcelain dish on a water bath. The precipitate of salts was filtered off and dissolved in the least possible amount of water; the solution was filtered and acidified with hydrochloric acid. The precipitated oil rapidly crystallized when the mixture was stirred, and 600 mg of a substance of m.p. 195-200° was obtained. Two recrystallizations from 50% aqueous acetone yielded 400 mg of the pure trans acid (XIX), m.p. 212-213° with decomposition.

	Found %:	C 65.62; 65.66; H 7.64; 7.81
$C_{13}H_{18}O_4$	Calculated %:	C 65.52; H 7.53

Hydrogenation of the Trans Acid (XIX)

The trans acid (XIX) (200 mg) was dissolved in glacial acetic acid (5 ml) and hydrogenated over platinum oxide, and one molecular proportion (20 ml) of hydrogen was absorbed. The catalyst was filtered off, and the solvent was removed under reduced pressure. When treated with water, the residue yielded a crystalline substance, m.p. 180-190°. Attempts to crystallize it from aqueous methanol or acetone did not result in the isolation of a pure individual product, a crystalline substance of extended melting range (180-190°) being obtained in all cases. This, however, was shown by analysis to have the composition of trans-decahydro-2-methyl-1,2-naphthalenecarboxylic acid (XX).

	Found %:	C 65.29; 65.27; H 8.36; 8.61
$C_{13}H_{22}O_4$	Calculated %:	C 65.01; H 8.33

Dimethyl Ester of cis-1,2,3,4,5,6,7,8-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XXI)

The cis diester (XVII) (950 mg) was added to 10 ml of a mixture of two parts of acetic anhydride and one part of glacial acetic acid saturated with dry hydrogen chloride, and the solution was heated at 60° for one hour. The solvents were driven off, and vacuum distillation of the residue yielded 750 mg of the cis diester (XXI), b.p. 145-146° (3 mm), n_D^{23} 1.4925.

	Found %:	C 67.38; 67.50; H 8.44; 8.36
$C_{15}H_{22}O_4$	Calculated %:	C 67.69; H 8.33

trans-1,2,3,4,5,6,7,8-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XXII)

By the procedure used for the isomerization of the cis diester (XVII), 700 mg of the cis diester (XXI) yielded 500 mg of a crystalline substance, m.p. 153-158°. Two recrystallizations (from 50% aqueous acetone and from 50% aqueous methanol) yielded the pure trans acid (XXII), having a constant m.p. of 173-174° with decomposition.

$C_{13}H_{18}O_4$ Found%: C 65.39; 65.49; H 7.51; 7.40
Calculated%: C 65.52; H 7.53

Found: M 234.4 (by titration with NaOH)
Calculated: M 238.3

The trans acid (XXII) gave a positive reaction with tetranitromethane and was not hydrogenated in presence of platinum oxide under the usual conditions.

SUMMARY

1. A study has been made of the diene condensation of 1-vinylcyclohexene (I) with citraconic anhydride (II), and it has been shown that in this reaction the ortho and meta adducts (III) and (IV) are formed in the proportions of 5 : 1 and in an overall yield of 92%. Hydrolysis of the cis anhydrides (III) and (IV) yielded the corresponding cis-1,2,3,5,6,7,8,8a-octahydromethyl-1,2-naphthalenedicarboxylic acids (V) and (VI), and the structures and spatial configurations of these have been proved.

2. The unsaturated cis anhydrides (III) and (IV), and also the corresponding cis acids (V) and (VI), are readily hydrogenated in a sterically selective manner at a platinum catalyst into the corresponding saturated compounds (VII), (VIII), (XV), and (XVI), the direction of the reaction being determined by the screening effect of the cis substituents at (C-1) −(C-8a) on the double bond.

3. By the isomerization of the cis diesters (IX), (X), and (XVII) with the aid of sodium methoxide, the corresponding trans acids (XI), (XII), and XIX) have been obtained in good yield, and this reaction may provide a convenient method for their synthesis. The hydrogenation of the unsaturated trans acid (XIX), unlike that of the isomeric trans acid (XI), is not sterically selective.

4. By treatment with acetyl chloride in a mixture of acetic anhydride and acetic acid, the cis diesters (IX) and (XVII) have been caused to undergo isomerization with displacement of the double bond to give the cis diesters (XIII) and (XXI). Further isomerization of these in presence of sodium methoxide yields the trans acids (XIV) and (XXII), which have an inter-ring double bond. These acids, as also the esters (XIII) and (XXI), cannot be hydrogenated over a platinum catalyst under the usual conditions.

5. Irrespective of the temperature (within the range 100-230°), the condensation of 1-vinylcylcohexene with citraconic anhydride proceeds by exo-addition.

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N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

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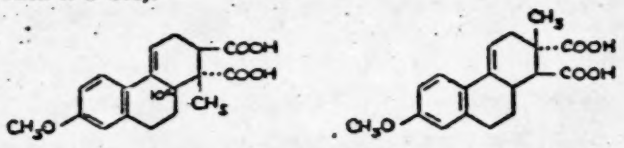
STEREOCHEMISTRY OF CYCLIC COMPOUNDS

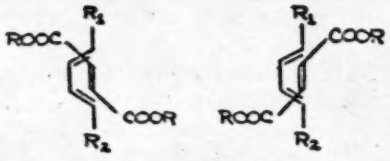
COMMUNICATION 5. CONDENSATION OF 1-VINYLCYCLOHEXENE WITH DIMETHYL MESACONATE

I. N. Nazarov, V. F. Kucherov, and V. M. Andreev

In spite of the large number of investigations devoted to the study of the diene condensation of trans dienophiles, only in isolated cases has the condensation of these with vinylcycloalkenes been investigated. The possibility of such a reaction was first noted in the case of the condensation of bicyclohexenyl with fumaric acid [1]. In 1951 Bachmann and Controulis [2] described the condensation of mesaconic acid with 1,2-dihydro-7-methoxy-4-vinylnaphthalene, which resulted in the formation of two trans structural isomers, the steric configurations of which were not proved (configuration at C-10a).



It may now be regarded as firmly established that the condensation of vinylcycloalkenes with trans dienophiles makes it possible to synthesize not only structural isomers, but also stereoisomers as has been observed on a number of occasions in the reactions of the simplest unsymmetrical dienes with certain trans dienophiles [3]. In diene condensations with trans dienophiles, the different orientations of the reactants are equally probable, so that the different stereoisomeric forms of the trans adducts can be formed:



The use in this reaction of various vinylcycloalkenes as unsymmetrical dienes can result in the formation of stereoisomeric forms of polycyclic compounds having a trans disposition of substituents.

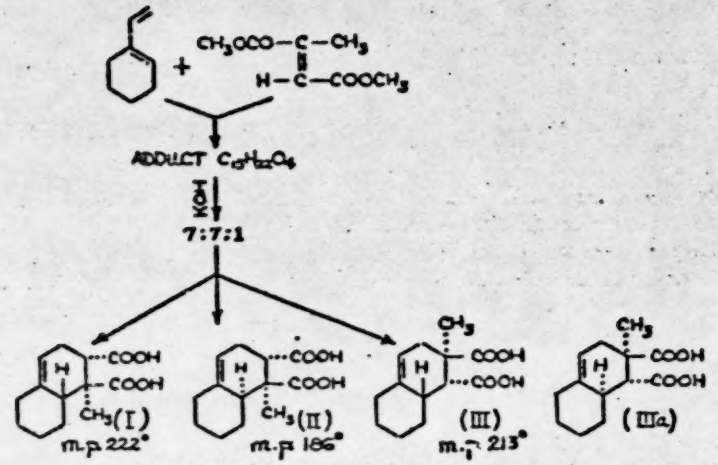
As the simplest example of a diene condensation of this type, we have studied the reaction of 1-vinylcyclohexene with dimethyl mesaconate. It was found that, when a mixture of dimethyl mesaconate and excess of 1-vinylcyclohexene (2-2.5 molecular proportions) was heated in benzene at 230-240° for four hours, a liquid adduct was formed (yield greater than 70%), a small amount of the dimer of 1-vinylcyclohexene being present as an impurity. At a lower temperature (120-140°) the reaction was much slower. Repeated vacuum fractionation yielded the pure liquid adduct, and analysis showed that it corresponded in composition to the expected condensation product $C_{15}H_{22}O_4$. In spite of its narrow boiling range, this product was not homogeneous, and its hydrolysis with 30% aqueous caustic potash, followed by fractional crystallization, yielded three individual crystalline acids (I), (II), and (III) in the proportions of 7 : 7 : 1 approximately. (See Scheme (A) on following page.)

It was not found possible to isolate the fourth possible isomer (IIIa), corresponding to the acid (III) with a different disposition of hydrogen at C-8a.

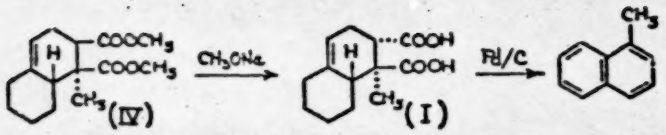
The acid (I) was found to be identical with trans-1,2,3,5,6,7,8,8a-octahydro-1-methyl-1,2-naphthalenedicarboxylic acid, which we prepared previously [4] by the isomerization of the corresponding cis diester (IV). When dehydrogenated in presence of palladized charcoal, this acid gave 1-methylnaphthalene. (See Scheme (B) on following page.)

The acid (III), which was formed in small amount, was found to be identical with the trans-1,2,3,5,6,7,8,8a-octahydro-2-methyl-1,2-naphthalenedicarboxylic acid obtained by the isomerization of the cis diester (V) and

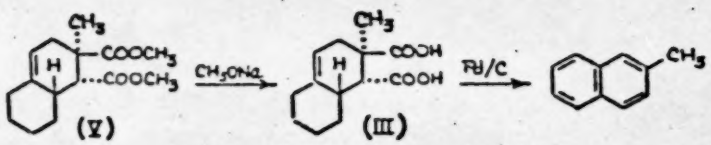
(A)



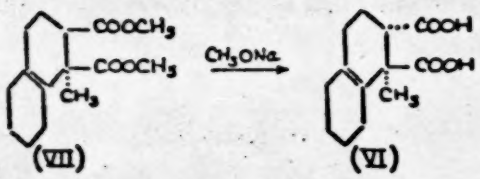
(B)



shown previously to have this structure by dehydrogenation to 2-methylnaphthalene [4].



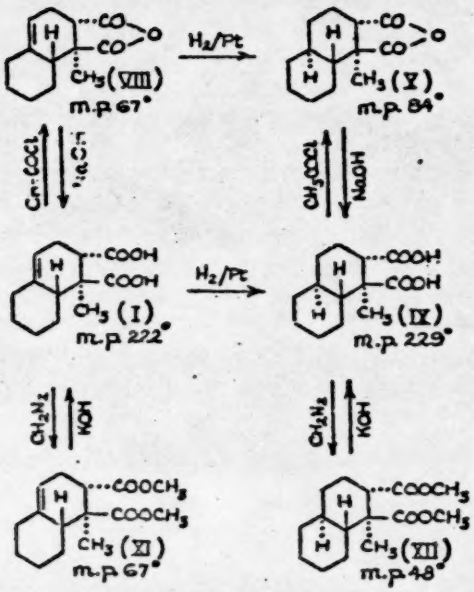
Dehydrogenation of the trans acid (II) over palladized charcoal again yielded 1-methylnaphthalene, so that its structure is similar to that of the trans acid (I). It was found, however, that the trans acid (II) was different from the trans acid (VI), which has an inter-ring double bond and has been prepared previously by us [4] by isomerization of the cis diester (VII):



The trans acids (I) and (II), therefore, have identical skeletons, and differ not in the position of the double bond, but only in the configuration of the hydrogen at C-8a.

We have studied some of the reactions of the three isomeric trans acids (I), (II), and (III). When the trans acid (I) was treated with acetyl chloride, it readily yielded the trans anhydride (VIII), m.p. 67°. Both the trans acid (I) itself and its anhydride (VIII) were readily hydrogenated in presence of a platinum catalyst with formation of the saturated trans acid (IX) and trans anhydride (X). The latter was formed also by the action of acetyl chloride on the saturated trans acid (IX). In this case an interesting feature of the hydrogenation was the formation of a single

saturated compound. This steric selectivity in the course of the hydrogenation is most probably to be explained by the presence of powerful simultaneous screening effects of the carboxyl group at C-1 and the hydrogen at C-8a, which exceed the screening effects of the methyl group at C-1 and the carboxyl at C-2; this view is supported by an examination of Stuart atomic models. Hence, hydrogenation of the compounds (I) and (VIII) should occur trans to the hydrogen at C-8a and to the carboxyl at C-1, and the hydrogenation products (IX) and (X) should have the configuration of trans-decahydronaphthalene.

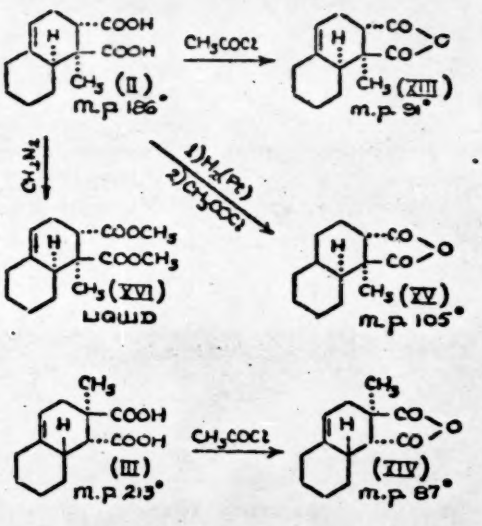


When treated with diazomethane, the trans acids (I) and (IX) give the corresponding trans diesters (XI) and (XII) in quantitative yield. The unsaturated trans diester (XI), unlike the corresponding diester of the cis series, cannot be caused to undergo isomerization in presence of acidic reagents with displacement of the double bond to the inter-ring position.

The trans acids (II) and (III) also readily give the trans anhydrides (XIII) and (XIV) under the action of acetyl chloride. In this case hydrogenation in presence of a platinum catalyst, both of the trans acids themselves and of their anhydrides, does not proceed in a selective manner, and therefore yields a mixture of isomers that is difficult to separate. Only in the case of the trans acid (II) was it found possible to isolate the individual saturated trans anhydride (XV), m.p. 105°, from the product obtained by treatment of the mixture of saturated acids with acetyl chloride, and the configuration of this at C-4a has not been established.

Atomic models of the trans acids (II) and (III) indicate that there is no preferential screening of the double bond by the substituents, and in this case hydrogenation goes in both of the possible directions.

The trans acid (II) is readily converted by diazomethane into the trans diester (XVI), which, like the trans diester (XI), is not capable of isomerization with displacement of the double bond to the inter-ring position, such as occurs in the case of the corresponding esters of the cis series.



EXPERIMENTAL

Condensation of 1-Vinylcyclohexene with Dimethyl Mesaconate

A mixture of 30 g of dimethyl mesaconate (b.p. 80° (5 mm); n_D^{23} 1.4550) [5], 50 g of 1-vinylcyclohexene, and 70 ml of cryoscopic benzene was heated in presence of 0.2 g of pyrogallol in a steel tube in an atmosphere of nitrogen at 230-240° for four hours. After removal of benzene, excess of 1-vinylcyclohexene, and a small amount of dimethyl mesaconate by distillation, the reaction product was vacuum-distilled and yielded 48.9 g of a thick oil, b.p. 135-150° (3.5 mm) and n_D^{20} 1.4998. Two vacuum fractionations yielded 37.2 g of adduct, b.p. 130-134° (2 mm) and n_D^{20} 1.4960. Yield 74% on the dimethyl mesaconate.

Found %: C 67.81, 67.70; H 8.57, 8.57

$C_{15}H_{22}O_4$ Calculated %: C 67.69, H 8.33

Hydrolysis of the Condensation Product

The adduct (17.5 g; b.p. 130-134° / 2 mm) was boiled with a solution of 30 g of caustic potash in 80 ml of water until solution was complete (five hours), and the solution was then heated in a steel tube at 130-135° for seven hours. The brown solution was treated with charcoal and filtered, and was then acidified to Congo Red with hydrochloric acid. The precipitated oil was extracted with ether, and the ether extract was dried with sodium sulfate. Ether was distilled off until the volume reached 40-50 ml, when crystals formed of an acid of m.p. 211-212° (3.5 g). These were filtered off, and the filtrate was evaporated to half bulk, when a further 0.5 g of the same acid, m.p. 207-210°, was isolated. Recrystallization from 70% aqueous methanol yielded 3.15 g of the trans acid (I), m.p. 221-222°, identical with that prepared previously by isomerization of the cis diester (IV) [4].

After separation of the trans acid (I), the ethereal mother liquor was evaporated under reduced pressure to half bulk, and 1.4 g of a trans acid of m.p. 181-184° was isolated. Addition to the ethereal filtrate of an equal volume of petroleum ether resulted in the separation of 1.8 g of the same acid, m.p. 178-182°. Recrystallization from 50% aqueous acetone yielded 3.05 g of the individual trans acid (II), m.p. 185-186° with decomposition.

Found %: C 65.67; 65.48; H 7.81; 7.69

$C_{13}H_{18}O_4$. Calculated %: C 65.52 H 7.53

After the mother liquor remaining after the separation of the trans acids (I) and (II) had stood for two months at room temperature, 2.2 g of a nonhomogeneous substance of m.p. 165-180° crystallized out; it was not found possible to isolate any individual substance from this. The liquid residue obtained after removal of solvents was dissolved in 4 ml of ether and diluted with an equal volume of petroleum ether. After two days, 0.7 g of a substance of m.p. 185-195° crystallized out from the solution, and this, after recrystallization from 50% aqueous methanol melted at 200-205° (0.5 g). A second recrystallization from 50% aqueous methanol yielded 0.4 g of the crystalline trans acid (III), m.p. 210-211°, undepressed by admixture of the acid obtained previously by the isomerization of the cis diester (V) [4].

Dehydrogenation of the Trans Acid (I)

A mixture of 1.1 g of the trans acid (I), m.p. 221-222°, 0.5 g of palladized charcoal (10% Pd), and 20 ml of cryoscopic benzene was heated in an autoclave in an atmosphere of nitrogen at 360-370° for 18 hours. The catalyst was filtered off, the benzene was distilled off, and the residue was distilled under atmospheric pressure, when 0.43 g of a hydrocarbon having n_D^{20} 1.5975 was obtained. Its picrate, prepared by the usual method, melted at 139.5-141°, and the melting point was not depressed by admixture of the picrate of 1-methylnaphthalene.

Dehydrogenation of the Trans Acid (II)

When treated by the above procedure, 1.0 g of the trans acid (II) of m.p. 185-186° yielded 0.35 g of a hydrocarbon having n_D^{28} 1.6040. Its picrate had a melting point of 140-141°, undepressed by admixture of the picrate of 1-methylnaphthalene.

Anhydride of trans-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (VIII)

The trans acid (I) (0.5 g) was boiled with acetyl chloride (5 ml) for two hours. The acetyl chloride was distilled off, and the residue was repeatedly evaporated down with benzene, and then with petroleum ether, until finally 0.44 g of a crystalline substance of m.p. 63-67° was obtained. Recrystallization from petroleum ether yielded the pure trans anhydride (VIII) in the form of rhombic crystals, m.p. 66-67°.

Found %: C 70.71; 70.74; H 7.34; 7.35

$C_{13}H_{16}O_3$. Calculated %: C 70.92; H 7.28

Hydrolysis of the trans anhydride (VIII) with 10% aqueous caustic soda gave a quantitative yield of the original trans acid (I).

Anhydride of trans-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (X)

The trans anhydride (VIII) (0.2 g) was dissolved in glacial acetic acid (5 ml) and hydrogenated over platinum oxide, when one molecular proportion of hydrogen (25 ml; 20° 751 mm) was absorbed. Acetic acid was distilled off under reduced pressure, and the liquid residue crystallized completely after being evaporated down with benzene, and then with petroleum ether. Recrystallization from petroleum ether yielded 0.14 g of the pure saturated trans anhydride (X), m.p. 83.5-84.5°.

Found %: C 70.12; 69.99; H 7.95; 7.90

$C_{13}H_{18}O_3$. Calculated %: C 70.21; H 8.15

trans-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (IX)

1. The trans acid (I) (0.4 g) was dissolved in glacial acetic acid (10 ml) and hydrogenated over platinum oxide, when one molecular proportion of hydrogen (50 ml; 26°, 743 mm) was absorbed in the course of three hours. Removal of solvent under reduced pressure yielded a crystalline product of m.p. 199-205°, and this, after recrystallization from 50% aqueous acetone, yielded 0.28 g of the saturated trans acid (IX), m.p. 227-228°, identical with the substance prepared previously [4].

2. The saturated trans anhydride (X) (0.35 g) was boiled with 3 ml of 5% aqueous caustic soda for ten minutes. The acid precipitated by acidification, which melted at 228-229° after crystallization from 50% aqueous acetone, was found to be identical with the trans acid (IX) obtained in the previous experiment. When boiled with acetyl chloride, the saturated trans acid (IX) readily yielded the saturated trans anhydride (X), m.p. 83-84°.

Dimethyl Ester of trans-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XI)

A suspension of 2.6 g of the trans acid (I) in 50 ml of ether was treated with excess of an ether solution of diazomethane. After removal of ether, 2.6 g of a crystalline substance, m.p. 61-62°, was obtained. Crystallization from a small amount of petroleum ether yielded the pure trans diester (XI), having a constant melting point of 62-63°. Hydrolysis of the trans diester (XII) with 40% aqueous caustic caustic potash gave the original trans-diester (I) in good yield.

Found %: C 67.77; 67.83; H 8.44; 8.45

$C_{15}H_{22}O_4$. Calculated %: C 67.69; H 8.33

Attempt to Effect Isomerization by Double-bond Displacement in the Trans Diester (XI)

The trans diester (XI) (2.0 g; m.p. 62-63°) was added to 20 ml of a mixture of two parts of acetic anhydride and one part of glacial acetic acid saturated with dry hydrogen chloride, and the solution was heated at 60° for 90 minutes. After removal of solvents, the liquid residue was vacuum-distilled, when it yielded 1.5 g of a colorless viscous liquid, b.p. 161-162° (5 mm) and n_D^{31} 1.4970, which gradually solidified. Crystallization from petroleum ether yielded 1.3 g of a crystalline substance, m.p. 61-63°, which was found to be identical with the original trans diester (XI).

Dimethyl Ester of trans-Decahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XII)

The saturated trans acid (IX) (0.6 g; m.p. 228-229°) was treated with excess of an ether solution of diazomethane, and the ether was distilled off. The liquid residue gradually crystallized when cooled, and after being washed on the filter with cold petroleum ether it melted at 46-48° (0.5 g). After crystallization from a small amount of petroleum ether, the saturated trans diester (XII) melted at 47-48°.

Found %: C 67.09; 67.15; H 9.02; 9.02

$C_{15}H_{24}O_4$. Calculated %: C 67.16; H 9.01

Hydrolysis of the trans diester (XII) with 40% aqueous caustic potash yielded the original trans acid (IX), m.p. 227-229°

Anhydride of trans-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XIII)

The trans acid (II) (0.2 g; m.p. 185-186°) was boiled with 2 ml of acetyl chloride for two hours. The acetyl chloride was distilled off, and the residue was heated under reduced pressure at 80-85° for 30 minutes to remove acetic anhydride. The liquid residue crystallized when treated with petroleum ether and cooled, and 0.1 g of glistening crystals of the trans anhydride (XIII) was obtained. The melting point, after crystallization from a small amount of petroleum ether, was 90.5-91.5°

Found %: C 70.98, 70.95; H 7.27, 7.39

$C_{13}H_{16}O_3$. Calculated %: C 70.92; H 7.28.

Hydrolysis of the trans anhydride (XIII) with 3% aqueous caustic soda yielded the original trans acid (II), m.p. 185-186°.

Hydrogenation of the Trans Acid (II)

The trans acid (II) (1.7 g) was dissolved in methanol (40 ml) and hydrogenated over platinum oxide in presence of a small amount of chloroplatinic acid. Hydrogenation was slow, and one molecular proportion of hydrogen

(173 ml) was absorbed in the course of four hours. Methanol was removed under reduced pressure, and a thick oil remained. This partially solidified when carefully rubbed out with petroleum ether. The crystalline product was filtered off and washed with a mixture of diethyl ether and petroleum ether (1 : 1). The product was 1.0 g of a substance of m.p. 183-190°. After two crystallizations from 50% aqueous methanol, the saturated trans acid did not have a sharp melting point (200-203°). It was a mixture of stereoisomers, and we were unsuccessful in separating them by crystallization.

	Found %:	C 65.25; 65.05; H 8.34; 8.39
$C_{13}H_{20}O_4$.	Calculated %:	C 65.01; H 8.33

This mixture (0.45 g; m.p. 200-203°) was converted into the anhydrides by treatment at the boil with acetyl chloride. With great difficulty the liquid residue remaining after removal of acetyl chloride was induced to crystallize: it was repeatedly evaporated down with benzene and with petroleum ether. Fractional crystallization from petroleum ether yielded 0.1 g of an individual saturated trans anhydride (XV), which crystallized in the form of glistening cubes, m.p. 104-105°.

	Found %:	C 70.39; 70.42; H 8.31, 8.04
$C_{13}H_{18}O_3$.	Calculated %:	C 70.21; H 8.15

Dimethyl Ester of trans-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (XVI)

A suspension of 1.5 g of the trans acid (II), m.p. 185-186°, in ether was treated with excess of an ether solution of diazomethane. Ether was distilled off, and vacuum distillation of the residue yielded 1.4 g of the trans diester (XVI) in the form of a colorless viscous oil, b.p. 152-153° (4 mm) and n_D^{22} 1.4975.

	Found %:	C 67.65; 67.66; H 8.34; 8.31
$C_{15}H_{22}O_4$.	Calculated %:	C 67.69 H 8.33

Hydrolysis of the trans ester (XVI) with 40% aqueous caustic potash yielded the original trans acid (II), m.p. 184-185°.

Attempt to Effect Isomerization by Double-bond Displacement in the Trans Diester (XVI)

A solution of 1.2 g of the trans diester (XVI) in 12 ml of a mixture of acetic anhydride and acetic acid saturated with dry hydrogen chloride was heated at 60° for 2 hours 30 minutes. The solvents were distilled off, and vacuum distillation of the liquid residue yielded 0.95 g of a thick oil, b.p. 161-162° (6 mm) and n_D^{22} 1.4980. Hydrolysis with 40% aqueous caustic potash yielded 0.8 g of a trans acid, and crystallization of this from 70% methanol yielded 0.6 g of m.p. 185-186°; it was found to be identical with the original trans acid (II).

Anhydride of trans-1,2,3,5,6,7,8,8a-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (XIV)

A mixture of 0.15 g of the trans acid (III), m.p. 212-213°, and 1.5 ml of acetyl chloride was boiled for one hour. The liquid reaction product remaining after removal of acetyl chloride was heated in a vacuum at 80-85° for 30 minutes. The residue, which gradually crystallized when treated with petroleum ether, was washed on the filter with a small amount of cold petroleum ether. The product was 0.11 g of the trans anhydride (XIV), which, after crystallization from petroleum ether, melted at 86-87°.

	Found %:	C 70.84; 70.85; H 7.15; 7.20
$C_{13}H_{16}O_3$.	Calculated %:	C 70.92; H 7.28

Hydrolysis of the trans anhydride (XIV) with 3% aqueous caustic soda gave a quantitative yield of the original trans acid (III), m.p. 212-213°.

SUMMARY

1. When 1-vinylcyclohexene was condensed with dimethyl mesaconate, three isomeric trans-1,2,3,5,6,7,8,8a-octahydromethyl-1,2-naphthalenedicarboxylic acids (I), (II), and (III) were isolated in the proportions of 7 : 7 : 1. The structures and spatial configurations of these acids have been proved.

2. The trans acids (I) and (II), which were obtained in equal amount, are of ortho structure and differ from one another only in the position of the hydrogen atom at C-8a. The trans acid (III), which was obtained in small amount, is a meta isomer in which the hydrogen at C-8a is trans with respect to the carboxyl at C-1.

3. It has been shown that the hydrogenation of the trans acid (I) and of its anhydride (VIII) in presence of platinum oxide proceeds in a selective manner with formation of the individual compounds (IX) and (X), whereas the trans acids (II) and (III) are not hydrogenated selectively under these conditions, but give mixtures of stereoisomers.

4. Such sterically selective hydrogenation of 1,2,3,5,6,7,8,8a-octahydromethyl-1,2-naphthalenedicarboxylic acids and their derivatives occurs only when the 8a-hydrogen and the 1-carboxyl are arranged cis to one another; this view is supported by an examination of atomic models.

5. The trans diesters (XI) and (XVI) are unable to undergo isomerization with displacement of the double bond to the inter-ring position, such as occurs in the case of the corresponding esters of the cis series.

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N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

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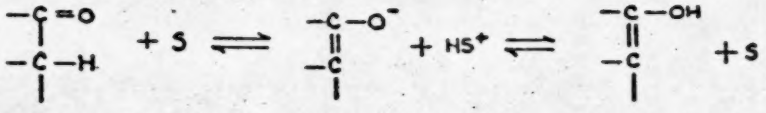
THEORY OF TAUTOMERIC EQUILIBRIUM IN SOLUTION

EFFECT OF SOLVATION ON THE EQUILIBRIUM BETWEEN THE KETO AND ISOMERIC CIS AND TRANS ENOL FORMS

M. I. Kabachnik

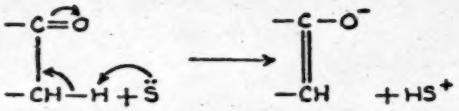
During recent years we have shown that the theory of acid-base protolytic equilibrium is applicable to prototropic tautomeric equilibrium [1]. By the use of this theory we have succeeded in deriving some important quantitative relationships characterizing keto-enol tautomeric equilibrium. These calculations were based on the concept of the ionization-protolysis mechanism of tautomeric change, which has been advanced at various times and in various forms by a number of authors, particularly Pedersen [2].

The results of numerous investigations on keto-enol tautomeric equilibrium in solution indicate that it is an acid-base equilibrium of two acids – the keto and enol forms which yield, by ionization, the same, common anions of enolate structure. Proton transfer from keto to enol and back is effected by the participation of proton-carrier molecules S, which can unite reversibly with a proton.

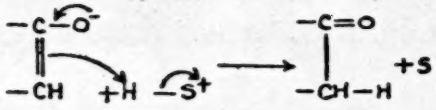


The part of proton carrier (S) may be played by any species having an affinity for a proton. This can be solvent molecules, if they have basic properties (water, alcohols, ethers), and solvent anions (hydroxyl anions in water, acetate anions in an acetic acid solution, which are known to have strongly basic properties); this can consist also of the molecules of any bases present in the solution (pyridine, amines, etc.). Finally, in aprotic solvents, such as benzene, carbon disulfide, and hydrocarbons, the part of proton carrier (S) may be played by the molecules of the keto-enol compound themselves, to an extent depending on their ability to unite with protons. In all cases the role of the species S is the same: to remove a proton from one place in an organic molecule (for example, from the methylene group of the keto form), and then to attach the proton to another place in the anion formed (for example, to the oxygen of the enolate ion), and vice versa.

In one of the stages of tautomeric change, the process proceeds with transfer of reaction center [3]. That is to say, in the



protolysis of the keto form, the anionic charge appears not on the carbon atom from which the proton goes, but on the oxygen atom at the other end of the conjugated system H–C–C = O. Also, in the recombination of the ions with formation of the keto form:



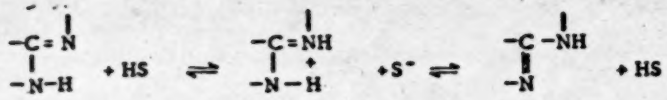
the proton unites not with the oxygen atom on which the anionic charge is concentrated (or almost entirely concentrated), but with the carbon atom at the other end of the conjugated system O–C = C.

Ionization of the enol form and the reverse recombination of ions in the direction of the enol form occur without transfer of reaction center: the ionic charge arises and subsequently disappears at the atom in the molecule from which the proton breaks away and to which it later returns. Protolysis of the enol form is rapid, whereas protolysis of the keto form (pseudoacid) is slow.

From the physicochemical point of view, keto-enol tautomeric equilibrium is a complex case of acid-base protolytic equilibrium in solution. It differs from ordinary acid-base equilibrium in two respects: in the first place,

there are two acids instead of one corresponding to one sort of anions, so that the anion has two different basicity constants (for addition of the proton at two different places in the anion); and, in the second place, one of the acids taking part in the equilibrium (the keto form) is a pseudoacid, which ionizes slowly. In other respects, keto-enol tautomeric equilibrium is subject to the same laws as the ionization equilibrium of the usual weak acids.

This concept of keto-enol tautomeric equilibrium is no doubt applicable also to other forms of prototropic equilibrium in substances of an acidic character. We must point out that the formation of a pseudoacid is not an essential feature of the tautomeric equilibria of acids: in lactim-lactam tautomerism, for example, both forms are true acids. We must point out also that such concepts must be applicable also to the prototropic tautomerism of substances of a basic nature. In this case, proton transfer is accompanied by the formation not of a common anion, but of a common cation, which arises from both tautomeric forms as the result of the addition of a proton to each of them at different ends of the conjugated system of atoms. This occurs, for example, in amidine tautomerism:



It may be considered that keto-enol tautomeric changes in acid media proceed by a similar mechanism (for example, in sulfuric acid solution [4]), and that this applies in general for the acid catalysis of keto-enol changes. We consider that the laws found for keto-enol equilibrium are of a general character, and may be extended, with some modifications, to other examples of tautomerism.

As we have shown, the application of the theory of acid-base protolytic equilibrium to the ternary buffer system:

$$KH + S \rightleftharpoons E^- + HS^+ \rightleftharpoons EH + S,$$

(in which KH represents the keto form, and EH the enol form) results (for dilute solutions) in a simple relationship between the tautomeric equilibrium constant K_{TS} and the ionization or protolysis constants of the keto and enol forms, treated as acids:

$$K_{TS} = \frac{[EH]}{[KH]} = \frac{K_{KS}}{K_{ES}} = \frac{K'_{KS}}{K'_{ES}} = \frac{K_K}{K_E} \cdot \frac{f_{KS}}{f_{ES}} \quad . \qquad (1)$$

([EH] and [KH] are the concentrations of the tautomers; K_{KS} and K_{ES} are the ionization constants of the keto and enol forms in the solvent S; K'_{KS} and K'_{ES} are the corresponding constants for protolysis by the base S; K_K and K_E are thermodynamic acidity constants; and f_{KS} and f_{ES} are activity coefficients*).

The tautomeric equilibrium constant is equal to the ratio of the ionization constants of the keto and enol forms in the given solvent (and also to the ratio of the protolysis constants); it is equal also to the ratio of the thermodynamic acidity constants of the keto and enol forms, multiplied by the ratio of the activity coefficients. The ratio of the thermodynamic acidity constants does not depend on the nature of the solvent; it may be termed the "thermodynamic constant" of tautomeric equilibrium K_t.

$$K_t = \frac{K_K}{K_E} \qquad (2)$$

It characterizes the "enolizability" of the tautomeric compound, quite apart from any effect due to the solvent. The higher the acidity constant of the keto form and the lower the acidity constant of the enol form, the higher the "enolizability" of the given tautomeric compound.

The ratio f_{KS}/f_{ES} expresses the effect of the solvent on the keto-enol tautomeric equilibrium, i.e. its "enolizing power". Here the most important factor is the nature of the solvation of the keto and enol forms by the given solvent. The higher the solvating effect of the solvent on the enol form (the undissociated molecule), the lower its activity coefficient and the greater the enolization in the given solvent; and vice versa.

In each case the position of equilibrium will be determined by both factors: the "enolizability" of the tautomeric compound, given by the value of K_t, and the "enolizing power" of the solvent f_{KS}/f_{ES}, which depends on the relative degrees of solvation of the forms. The position of tautomeric equilibrium is always found to be displaced in the direction of the form that is the less acidic in the given medium.

* Activities being related to a standard state that is the same for all solvents.

At very low values of K_t (acidity constant of the keto form much less than that of the enol), the substance is practically completely "ketonized" in all solvents. An example of a substance of this type is acetone ($K_{T,H_2O} = 2.5 \cdot 10^{-9}$); in aqueous solution acetone contains 0.00025% of enol form, and in hexane – the most "enolizing" solvent – the content of the enol form of acetone cannot exceed 0.06%. At very high values of K_t (acidity constant of the keto form many times as great as that of the enol form), the substance consists of almost 100% enol in all solvents. An example of substances of this second type is dimedone, which is practically completely enolized.

At intermediate values of K_t the position of tautomeric equilibrium is extremely dependent on the nature of the solvent, which displaces equilibrium in the direction of the most readily solvated form. When $K_t = 1$, i.e. when $K_K = K_E$, the position of equilibrium is entirely determined by the relative degrees of solvation of the forms. When solvents are arranged in a series according to the enolizing abilities (which corresponds only approximately with the series arranged according to the value of the dielectric constant), it is found that, in the more polar solvents the less solvated enol forms are stronger acids than the corresponding keto forms; the values of the equilibrium constant K_{TS} are correspondingly low. As we pass to the less polar solvents, which solvate the enol forms more strongly, this difference is first eliminated (the equilibrium constant passes through unity: $K_{KS} = K_{ES}$), and then the keto forms become the stronger acids ($K_{TS} > 1$). The table gives Meyer's results [5], which illustrate this behavior.

In the table, the bold stepped line separates the region in which the enol forms are more acid than the keto forms (upper left part of the table) from that in which the keto forms are more acid than the enol forms (lower right part of the table).

The effect of the solvent on the position of keto-enol tautomeric equilibrium can be treated quantitatively. Thus, the application to keto-enol equilibrium, as an equilibrium of the protolytic acid-base type, of the well-known Brönsted formula [6]

$$pK_{AS_1} = pK_{AS_2} + \text{const}^{*}, \tag{3}$$

together with the rules formulated by Izmailov [7], results in the important relationship

$$pK_{TS_1} = pK_{TS_2} + \text{const}', \tag{4}$$

which is valid for all keto-enol tautomeric substances in any two solvents S_1 and S_2, and which has been well confirmed experimentally. It follows from this formula that the value of f_{KS}/f_{ES}, which characterizes the enolizing power of the solvent, is constant for all keto-enol tautomeric substances. This constant is characteristic for each solvent with respect to a given class of tautomeric substances (in the case under examination – the keto-enol class).

Equation 4, after some simple transformations [8], yields the equation due to Meyer

$$K_{TS} = \mathcal{E} \cdot \mathcal{L}, \tag{5}$$

which he deduced by an empirical method [9].

According to Meyer, a measure of the enolizability of a keto-enol compound is afforded by the value of $\mathcal{E}$, which is equal to the ratio of the equilibrium constant of the given keto-enol compound to that of acetoacetic ester in the same solvent. The value of $\mathcal{L}$ is a measure of the enolizing power of the solvent; it is equal to the equilibrium constant of acetoacetic ester in the given solvent. It can be shown that the constant $\mathcal{E}$ in Meyer's equation is equal to the ratio of the thermodynamic equilibrium constants of the given keto-enol compound (K_t) and acetoacetic ester (K_t°).

$$\mathcal{E} = K_t / K_t^{\circ} \tag{6}$$

This quantity, of course, does not depend on the nature of the solvent. Meyer's constant $\mathcal{L}$ is also readily expressed in terms of the physicochemical constants of the keto and enol forms in the given solvent:

$$\mathcal{L} = K_t^{\circ} \cdot \frac{f_{KS}}{f_{ES}}$$

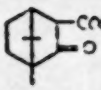
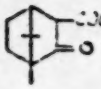
Hence, the constants in Meyer's equation differ from those in Equation 1 by the presence of the constant factor K_t°.

Experiment confirms these ideas. The keto and enol forms, being acids, may be titrated in solution, e.g. potentiometrically; and their ionization constants can therefore be determined. An investigation carried out by Kabachnik and Ioffe [10] has confirmed the applicability of Brönsted's formula (Equation 3) to the keto and enol forms, regarded as acids. The empirical ionization constants were determined potentiometrically with the aid of a glass electrode

* $pK = -\log K$.

TABLE

Values of K_{TS} for Some Keto-Enol Tautomeric Substances (Meyer [5])

Substance \ Solvent	H_2O	HCOOH	67% CH_3OH	CH_3COOH	CH_3OH	CH_3COCH_3	$CHCl_3$	C_2H_5OH	$CH_3COOC_2H_5$	C_6H_6	$C_6H_5CH_3$	$(C_2H_5)_2O$	CS_2	C_6H_{14}
$CH_3COCH_2COOC_2H_5$	0.004	0.011	0.023	0.061	0.074	0.08	0.089	0.13	0.15	0.22	0.26	0.43	0.73	1.00
$CH_3COCH_2CONHC_6H_5$	–	–	0.026	0.076	0.09	–	0.09	0.18	0.33	0.15	0.19	0.80	–	–
$C_6H_5COCH_2COOCH_3$	0.003	0.028	0.046	0.16	0.16	0.18	0.18	0.32	0.33	0.45	0.62	0.90	1.6	2.2
	–	0.15	0.25	0.50	0.55	–	–	0.92	0.95	–	–	2.6	–	–
	–	–	–	–	0.87	0.85	–	1.7	2.0	–	–	6.5	–	–
$CH_3COCH_2COCH_3$	0.22	–	0.90	2.8	2.6	2.2	3.8	4.0	3.1	5.7	7.0	16	15	12
$C_6H_5COCH_2COCH_3$	–	2.3	2.5	8	9	10	13	14	–	–	–	–	–	–
$(C_6H_5CO)_2CHCOCH_3$	–	–	–	6	6	–	–	10	–	–	30	–	–	–
$C_6H_5COCH_2COC_6H_5$	–	4	–	24	22	–	–	40	–	–	–	–	–	–

for a number of equilibrium keto-enol substances ($K_{KE,S}$) dissolved in water and in 70% dioxane. These empirical ionization constants are related to the corresponding constants of the pure forms by the equation

$$K_{KE,S} = \frac{K_{KS}K_{ES}}{K_{KS} + K_{ES}}. \qquad (8)$$

The equilibrium constants K_{TS} were then determined bromometrically by the Meyer-Dieckmann method, and the ionization constants of the separate forms were calculated from these tautomeric equilibrium constants (K_{TS}) and the empirical ionization constants for the equilibrium mixture ($K_{KE,S}$) by the equations:

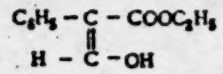
$$K_{KS} = K_{KE,S}(K_{TS} + 1); \qquad (9) \qquad K_{ES} = K_{KE,S}\,\frac{K_{TS} + 1}{K_{TS}}. \qquad (10)$$

It was found that in aqueous solution the enol forms were generally stronger acids than the keto forms. In 70% aqueous dioxane, however, the position was often the reverse; thus, in this solvent the keto form of benzoylacetone (1-phenyl-1,3-butanedione; $K_{KS} = 1.3 \cdot 10^{-10}$) is more acid than the enol form ($K_{ES} = 3.05 \cdot 10^{-11}$). The pK_{AS} values of keto and enol forms in water and aqueous dioxane are in good accord with the linear relationship required by Equation 3.

The empirical acidity of the solution is mainly determined by the less acid form, and the position of equilibrium by the ratio of the ionization constants of the two forms. In this way the question that has long troubled chemists – the connection between the acidity of solutions of keto-enol tautomeric substances, their enolizability, and the solvation of the tautomeric forms – is now resolved.

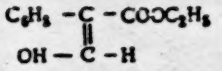
The above-cited calculations on tautomeric equilibrium, however, can characterize it only to the first approximation. In these calculations the equilibrium is considered without taking into account the possibility of cis-trans isomerism in the enol form, although such isomerism actually occurs. In some cases – in the case of phenylmalonaldehydic ester, for example – it has been found possible to effect the separation of the two stereoisomeric forms of the

enol (I and II) [11]: the cis form (α - form) is characterized by the ability to give a color with ferric chloride and to form a characteristic copper complex: the trans form (γ - form) does not possess this ability; both forms readily react with bromine, which indicates that they are both enols:



(I)

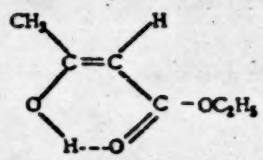
α - ester (liquid)



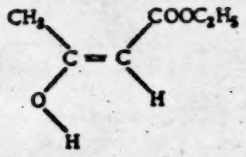
(II)

γ - ester (m.p. 110°)

According to Sidgwick [12], there is every reason to suppose that the well known enol form of acetoacetic ester of b.p. 33° (2 mm) is the cis form (III), and not the trans form (IV), its structure being characterized by the presence of an intramolecular hydrogen bond:



(III)



(IV)

Being an internal-complex compound, the cis enol form of acetoacetic ester has a lower boiling point (the keto form boils at 40-41° at 2 mm) and lower water-solubility (about 20 times as low) than the keto form; its Raman spectrum [13] is characteristic for a compound having an intramolecular hydrogen bond. Equilibrium acetoacetic ester contains not only the cis enol, but also some trans enol form [14]. The existence of enol forms in the trans configuration has been established by Henecka in a number of cases by a method depending on the inability of these enol forms to give a ferric chloride reaction [15]

There is therefore every reason to suppose that in solutions of keto-enol tautomeric substances three forms are present in equilibrium: the keto, cis enol, and trans enol forms. The equilibrium between the cis and trans enol forms must depend greatly on the nature of the solvent. Since the cis forms have internal-complex structures (intramolecular hydrogen bond) and are therefore of higher solubility in nonpolar solvents, and the trans forms have free hydroxyl groups and are of higher solubility in polar solvents, it would be expected, in accordance with the Van't Hoff-Dimroth rule, that polar solvents would displace the equilibrium in the direction of the trans form, and nonpolar in the direction of the less polar cis form. In those cases in which cis-trans isomers have been isolated, this has been found to be true: the trans enol form of phenylmalonaldehydic ester, which crystallizes from aqueous solution, rearranges into the cis form when transferred to a hydrophobic solvent (hexane, carbon disulfide [11, 16]). A solution of phenylmalonaldehydic ester in methanol or ethanol contains mainly the trans enol form, since it gives no reaction with ferric chloride [11].

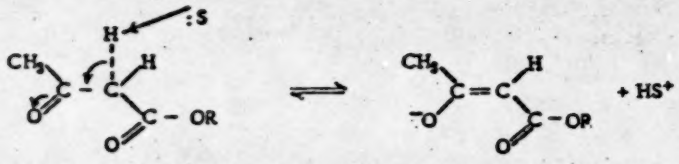
When, however, equilibrium between all of the three forms is examined (keto, cis enol, and trans enol), the relationship becomes less clear. As was pointed out for the first time by Arndt, Loewe, and Ginkök [17], it would be expected that nonpolar solvents would displace the equilibrium in the direction of the least polar form, which is readily solvated by hydrophobic solvents, i.e. in the direction of the cis enol form; this is actually observed. Polar solvents, however, should, according to these authors, displace the equilibrium in the direction of the form that is most readily solvated by polar solvents, i.e. in the direction of the trans enol form. In actual fact polar solvents displace the equilibrium in the direction of the keto form. The question "why not the trans enol ?" was examined thoroughly by these authors. They consider that the contradiction can be resolved by assuming that the keto forms can be hydrated in an aqueous medium with formation of hydrates (methylene glycols) and can be similarly converted into hemiacetals in an alcoholic medium. These hydrates and hemiacetals can be formed also from enol forms by addition of water and of alcohols. The hydrate and hemiacetal forms of the keto compounds should be more readily solvated by polar solvents than the trans enol forms, so that polar solvents will displace the equilibrium not towards the trans enol forms, but towards the hydrate of hemiacetal keto form. The authors found confirmation for this supposition in the fact that the hydrates of some keto forms are stable and isolable; thus the methyl hemiacetal of phenylmalonaldehydic ester is known [18].

It is, however, difficult to agree with the explanation of Arndt, Loewe, and Ginkök In the first place, displacement of equilibrium towards the keto form can be brought about not only by water and alcohols, but also by other polar solvents. As will be seen from the table, for any keto-enol tautomeric substance the content of keto form is greater in acetone solution than in ethanol solution. This fact is difficult to reconcile with the hypothesis of the formation of hydrates or hemiacetals. In the second place, it is important to note that it is in just those cases in which

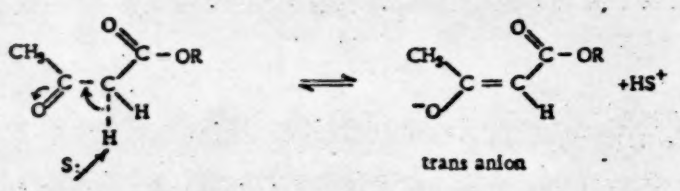
hydrate or hemiacetal formation actually does occur that departures from Meyer's rule [19] are observed, whereas Arndt and coworkers invoke the formation of hydrates or hemiacetals in order to explain the observance of this rule. We will further cite the just remarks of Briegleb and Strohmeyer [20], who pointed out that the views of Arndt and coworkers are in conflict with the fact that many keto-enol tautomeric substances (not only cyclic, but also straight-chain compounds such as malonaldehyde) contain more than 90% of enol form (mainly trans) in aqueous solution, and so do not form hydrates of the keto forms. Finally, if the formation of hydrates of the keto forms, in equilibrium with the enol forms, really does determine the displacement of equilibrium towards the keto forms in aqueous and alcoholic media, then increase in pressure should produce a still greater displacement of the equilibrium towards the hydrated keto forms (i.e. a reduction in the total number of molecules). However, according to the work of Kabachnik, Yakushkina, and Kislyakova [21], increase in pressure to 3000 atm results in only a slight displacement of the equilibrium, this displacement, however, being in the direction of the enol (mainly trans enol) forms.

It follows from these considerations that hydrate or hemiacetal formation is not the cause of the displacement of tautomeric equilibrium towards the keto forms in polar solvents. The actual causes of this phenomenon must be sought not in side reactions that complicate the process of tautomeric change, but in the process itself, in its relation to the solvation of the species present and their ionization.

We consider that the tautomeric equilibrium of cis and trans enol and keto forms is again an acid-base protolytic equilibrium; it differs from the equilibrium considered above in that three acids, not two (keto and enol) are in equilibrium: keto, cis enol, and trans enol, the cis-trans conversion of the enol form being effected through the keto form. If we examine the process of removing a proton from the keto form by means of the protophilic species S, it is found that, depending on the spatial disposition of the two carbonyls of the keto form of a 1,3-dicarbonyl compound (taken up in the course of free or restricted rotation about a C–C bond), the structure of the anion formed may be either cis or trans:



cis anion



trans anion

The complex acid-base equilibrium in the solution of the keto-enol compound may be represented schematically as

$$E_CH + S \rightleftharpoons E_C^- + HS^+ \rightleftharpoons KH + S \rightleftharpoons E_T^- + HS^+ \rightleftharpoons E_TH + S$$

(E_CH and E_TH are the cis and trans enols, and E_C^- and E_T^- are the corresponding anions). Following Brönsted, we may write for the ionization constants of the enol forms:

$$K_{E_CS} = \frac{[E_C^-]\,(HS^+)}{[E_CH]} = \frac{(E_C^-)\,(HS^+)}{(E_CH)} \frac{f_{E_CS}}{f_{E_C^-S}} = K_{E_C} \frac{f_{E_CS}}{f_{E_C^-S}} \qquad (11)$$

$$K_{E_TS} = \frac{[E_T^-]\,(HS^+)}{[E_TH]} = \frac{(E_C^-)\,(HS^+)}{(E_TH)} \frac{f_{E_TS}}{f_{E_T^-S}} = K_{E_T} \frac{f_{E_TS}}{f_{E_T^-S}} \qquad (12)$$

(the parentheses indicate activity and the brackets concentration). For the keto form we may write two ionization constants – for formation of the cis anion, and for formation of the trans anion:

$$K_{K_C S} = \frac{[E_C^-](HS^+)}{[KH]} = \frac{(E_C^-)(HS^+)}{(KH)} \frac{f_{KS}}{f_{E_C^- S}} = K_{K_C} \frac{f_{KS}}{f_{E_C^- S}} \quad (13)$$

$$K_{K_T S} = \frac{[E_T^-](HS^+)}{[KH]} = \frac{(E_T^-)(HS^+)}{[KH]} \frac{f_{KS}}{f_{E_T^- S}} = K_{K_T} \frac{f_{KS}}{f_{E_T^- S}} \quad (14)$$

From which it follows that

$$K_{TS} = \frac{[E_T H]}{[E_C H]} \frac{K_{E_C S} K_{K_T S}}{K_{E_T S} K_{K_S S}} = \frac{K_{E_C} K_{K_T}}{K_{E_T} K_{K_C}} \frac{f_{E_C S}}{f_{E_T S}} \quad (15)$$

The constant for the tautomeric cis-trans enol equilibrium depends not only on the ionization constants of these forms, but also on the ratio of the ionization constants of the keto form for cis- and trans-anion formation. Here again the equilibrium constant is defined as the product of two factors: the "thermodynamic equilibrium constant"

$$K_r = \frac{K_{E_C} K_{K_T}}{K_{E_T} K_{K_C}} \quad (16)$$

which does not depend on the nature of the solvent, and the solvation factor $f_{E_C S} / f_{E_T S}$.

The effect of the thermodynamic equilibrium constant is such that the higher the relative value of the acidity constant of the trans enol and the lower the acidity constant of the keto form for trans-anion formation, the more will the equilibrium be displaced towards the cis enol form; and vice versa.

The position of the equilibrium of cis and trans enol forms is determined by the simultaneous action of both factors

$$K_{TS} = K \frac{f_{E_C S}}{f_{E_T S}} \quad (17)$$

We may point out that the activity coefficient of the keto form does not enter into the expression for the constant K_{TS}; in other words, the ratio of the concentrations of the cis and trans enol forms in any solvent is independent of the solvation of the keto form by that solvent, but depends on the relative degrees of solvation of the cis and trans enol forms themselves.

The experimental (bromometric) determination of the content of enol form in solution gives the sum of the concentrations of cis and trans enol forms, and the empirical constant for keto-enol tautomeric equilibrium is

$$K_{TS} = \frac{[E_C H] + [E_T H]}{[KH]} . \quad (18)$$

It is easy to show that for this constant

$$K_{TS} = \frac{K_C S}{K_{E_C S}} \frac{K_T S}{K_{E_T S}} . \quad (19)$$

If one of the forms, e.g. the trans enol form, has an ionization constant that greatly exceeds those of the two other forms, then the term containing this ionization constant in the denominator can be neglected, and the equilibrium

constant is determined by the ratio of the ionization constants of the keto and second enol (cis) forms, i.e. by Equation 1.

The concepts developed above enable us to understand the relationships found by experiment. Let us take acetoacetic ester and acetylacetone (2,4-pentanedione) as examples. It must be supposed that the trans enol forms of acetoacetic ester and acetylacetone are stronger acids than the cis enol forms. They should be characterized by higher thermodynamic acidity constants and a greater tendency to be solvated by polar solvents. The cis enol forms are weaker acids; they are less readily solvated by polar solvents than by nonpolar solvents. This results from the presence in the cis enol forms of intramolecular hydrogen bonds, which stabilize the undissociated molecules and give them the properties of internal-complex compounds, which are more readily solvated by nonpolar solvents.

Experiments described in a paper by Eistert, Arndt, Loewe, and Ayca [22] confirm these views: in ether solution, containing mainly the cis enol form, acetylacetone is methylated only very slowly with diazomethane with formation of the ether of the cis enol; in methanol solution, in which much of the trans enol form should be present, acetylacetone reacts rapidly with diazomethane with formation of a mixture of cis and trans ethers.

As regards the keto form, in the case of acetoacetic ester the keto form is a weaker acid than the enol in all solvents except hexane. In the case of acetylacetone, this is true only for solutions in water and other strongly polar solvents. Already in a methanol medium, the keto form is found to be a stronger acid than the enol forms (or at least the cis enol form) (see the table). The keto forms are solvated more readily by polar than by nonpolar solvents, although they are solvated fairly well by the latter – they are not worse than the cis enol forms in this respect. This view finds support in the fact that for acetoacetic ester the content of keto form in almost all solvents is higher than in the vapor phase [according to Briegleb and Strohmeyer [20], at 20° the gas phase contains 48.0% of the keto form of acetoacetic ester ($K_T = 1.1$)]: and for acetylacetone in all solvents from water to toluene (see table) the content of keto form is higher than in the gas phase [according to Briegleb and Strohmeyer, at 20° the gas phase contains 6.3% of the keto form ($K_T = 14.9$)]: and only in ether and carbon disulfide solutions is the content of keto form approximately the same as in the gas phase.

Whatever the solvent may be, there can be little trans enol form present at equilibrium (since its thermodynamic acidity constant is high). In nonpolar solvents the equilibrium should be displaced towards the cis enol form: it is solvated more readily in these media, and the difference in acidic properties between it and the keto form disappears in the case of acetoacetic ester, and is reversed in direction in the case of acetylacetone. This displacement of equilibrium in nonpolar solvents in the direction of the cis enol form is indeed observed experimentally. In polar solvents the equilibrium should be displaced towards the trans enol and keto forms, as being more readily solvated. Owing to its high thermodynamic acidity constant, the trans enol form will be present in low equilibrium concentration; the solution will contain mainly the keto form. The enol fraction of the solution, however, must be greatly enriched in trans form. The experimental facts are in accord with this view. An equilibrium aqueous solution of acetoacetic ester contains 0.4% of the enol form, but it does not immediately give the ferric chloride reaction that is characteristic of the cis form, but only after some time, which will permit tautomeric change to occur. This 0.4%, therefore, consists mainly of trans form.

Increase in pressure should displace the equilibrium towards the most solvated form. In aqueous solution (and in other polar solvents) this is the trans enol form. Actually, according to our results, as the pressure is raised the content of the enol form (trans!) in aqueous solution increases (to 1.63% [21]). In chloroform and toluene solutions the most solvated form is the keto form. Increase in pressure, therefore, should displace the equilibrium in these solutions towards the keto form. Experiment shows that, when a pressure of 3000 atm is applied, the contents of enol form fall from 9 and 25 to 7 and 22%, respectively.

Hence, on the basis of the treatment of tautomeric equilibrium as protolytic acid-base equilibrium, a satisfactory explanation can be given of the experimentally observed relationships between the keto and cis and trans enol forms. This concept of tautomeric equilibrium can serve as a basis for further investigations.

SUMMARY

1. Keto-enol tautomeric equilibrium in solution has been examined from the point of view of the theory of protolytic acid-base equilibrium.

2. It has been shown that in solutions of open-chain keto-enol tautomeric substances three acids participate in the equilibrium: the keto form, the cis enol form, and the trans enol form. There are two anions corresponding to these three acids: the cis enolate and the trans enolate.

3. On the basis of the theory of acid-base equilibrium, an explanation has been advanced for the properties of such solutions.

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N. D. Zelinsky Institute of Organic Chemistry and
Institute of Heterorganic Compounds of the
USSR Academy of Sciences

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HIGH-TEMPERATURE CONTACT-CATALYSIS REACTIONS OF BENZENE AND ITS CLOSEST HOMOLOGS IN PRESENCE OF HYDROGEN AT HIGH PRESSURE

N. I. Shuikin and N. G. Berdnikova

A number of investigations [1, 2, 3, 4] have been devoted to the study of the behavior of aromatic hydrocarbons in presence of various catalysts at high temperatures. Great interest is presented by investigations directed to the study of alkylation and dealkylation reactions of aromatic hydrocarbons [5, 6, 7, 8].

As is well known, benzene and its closest homologs possess high thermal stability. Even under severe thermal conditions, the main process is the elimination of alkyl groups as the corresponding alkenes [1, 2, 3].

When hydrogen is present under high pressure (140-200 atm), benzene homologs undergo reaction in two main directions at 440-480°: hydrogenation to the corresponding cycloalkanes, and hydrogenolysis with elimination of side chains. Under destructive hydrogenation conditions, toluene loses its CH_3 group already at 460°. Thus, according to Hofmann and Lang's results [9], at 470° toluene yields 28% of benzene. By the hydrogenation of toluene at 490°, Laider and Szayne [10] obtained 25% of benzene. Prokonets, Filaretov, and Bogoslavskaya [11] submitted benzene to destructive hydrogenation in presence of MoS_2 and hydrogen at 200 atm and at 400-470°; in the catalyzate they found methylcyclopentane, cyclohexane, and branched-chain alkanes. Similar results were obtained also by Puchkov [12] in experiments on the destructive hydrogenation of benzene in presence of hydrogen at 140 atm. Maslyansky [13] studied the reactions of benzene in presence of MoS_2 a. hydrogen at 200 atm at a temperature of 500-550°, and his catalyzate contained cyclohexane, methylcyclohexane, cyclopentane, and branched alkanes (pentane and hexane isomers).

The reactions of cumene at 459° in presence of a metal oxide catalyst and hydrogen at 35 atm have been studied by Haensel and Donaldson [14]. In the catalyzate they found 1.2% of toluene, 19% of benzene, 0.9% of xylenes, and 12.3% of cycloalkanes. Among the various reactions occurring in this process, hydrogenolysis of the side chain with formation of benzene and propane predominated.

In previous papers [15, 16] we have described the results of investigations of the high-temperature contact-catalysis reactions of individual cycloalkanes and alkanes in presence of hydrogen at high pressure. On the basis of these experimental results, we have advanced hypotheses concerning the nature and direction of the reactions occurring in presence of hydrogen at high pressure and in contact with platinized aluminum oxide.

With a view to the further development of these studies, and also in order to elucidate certain peculiarities in the transformations of individual hydrocarbons, we considered it desirable to make a more detailed study of the behavior of aromatic hydrocarbons under our selected conditions. In the present investigation we have treated benzene, toluene, and ethylbenzene in presence of platinized aluminum oxide (4.5% Pt) under 20 atm of hydrogen at 460° at a space velocity of 0.43 liter/liter·hr, the molar ratio of hydrogen to hydrocarbon being 5:1.

EXPERIMENTAL

The properties of the original hydrocarbons, which were carefully purified and distilled over sodium through a column having an efficiency of about 100 theoretical plates, are given in Table 1.

TABLE 1

Properties of the Original Aromatic Hydrocarbons

Hydrocarbon	B. p. (corrected; °C)	n_D^{20}	d_4^{20}
Benzene	80.1	1.5010	0.8785
Toluene	110.5	1.4962	0.8668
Ethylbenzene	136-136.5	1.4960	0.8675

The experiments with these hydrocarbons were carried out in an apparatus of the continuous-flow type. The adjustment of the apparatus, the experimental procedure, and the analysis of the reaction products have been described

previously [15,16]. In order that the investigation of the components of the catalyzate might be as complete and reliable as possible, we took 850 g of each hydrocarbon.

Catalytic Treatment of Benzene

Benzene was brought into contact with platinized alumina at 460° at a space velocity of 0.43 liter/liter·hr. in presence of hydrogen at a pressure of 20 atm. A yield of 835.6 g (98.3%) of catalyzate was obtained (n_D^{20} 1.4980; d_4^{20} 0.8661). The fractionation of 800 g of this catalyzate was carried out at 756 mm through a 100-plate column, and the results are given in Table 2.

TABLE 2

Fractional Composition of the Benzene Catalyzate

Fraction No.	Boiling range of fraction (°C)	Amount of [illegible]	n_D^{20}	d_4^{20}	Yield (% on amount of catalyzate taken for fractionation)
I	27.5 - 29.3	2.5	1.3545	0.6207	0.3
II	29.3 - 36.5	3.4	1.3575	0.6263	0.42
III	36.5 - 50.5	5.2	1.3985	0.7448	0.65
IV	50.5 - 79.5	5.3	1.4720	0.7989	0.66
V	79.5 - 80.5	774.9	1.5010	0.8788	96.8
VI	80.5 - 110.5	—	1.4980	—	—
VII	110.5 - 111.0	1.56	1.4965	0.8664	0.2
VIII	111.0 - 150.0	2.4	1.4960	0.8571	0.30
	Residue	5.3	1.5235	—	0.66

As will be seen from the results in Table 2, Fractions I and II consisted, according to their properties, of isopentane and pentane [17] respectively. Fraction III was investigated with the aid of Raman spectra, and the results showed that the principal components of this fraction were pentane (20%), cyclopentane (75%), and a small amount of methylcyclopentane. Fraction IV, boiling range 50.5 - 79.5°, was submitted to chromatographic adsorption on silica gel, which yielded 4.2 ml of benzene and 2.4 ml of naphthenes and paraffins having n_D^{20} 1.4140 and d_4^{20} 0.7478. Optical (Raman) analysis showed the presence of methylcyclopentane (75%), branched hexanes (15%), and cyclohexane (qualitatively). The properties of Fractions V and VII indicated that they consisted of benzene and toluene respectively. Fraction VIII (2.4 g) was submitted to Ullmann permanganate oxidation [18], and from the mixture of acids obtained the following acids were isolated by the procedure developed by Moldavsky and coworkers [19]: benzoic acid (m.p. 121°), phthalic acid (0.5 g, m.p. 190°), isophthalic acid (1.67 g), and terephthalic acid (0.61 g). The last two acids were converted into their methyl esters, which melted at 65° and 140° respectively. The residue (6.2 g) was fractionated from a Favorsky flask at 754 mm, and yielded:

Fraction I B. p. 150 - 195°; 0.7 g; n_D^{20} 1.4980; d_4^{20} 0.8540

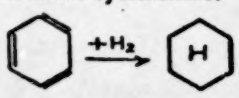
Fraction II B. p. 195 - 210°; 2.1 g; n_D^{20} 1.5185 —

Fraction III B. p. 210 - 230°; 3.0 g; n_D^{20} 1.5295 —

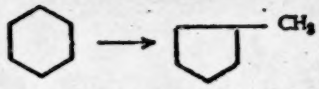
Residue and losses 0.4 g

Fraction I (b.p. 150-195°) was not investigated further owing to the inadequate amount of material available. Part of Fraction II (b.p. 195-210°) (1 g) was heated with picric acid in a water bath, when 0.6 g of a picrate of m.p. 148.5° was obtained, which indicates the presence of naphthalene in this fraction. Fraction III (b.p. 210-230°) solidified to a crystalline mass when cool; white crystalline plates, m.p. 81°, were obtained from this substance by sublimation, and judging from its properties, the substance was biphenyl.

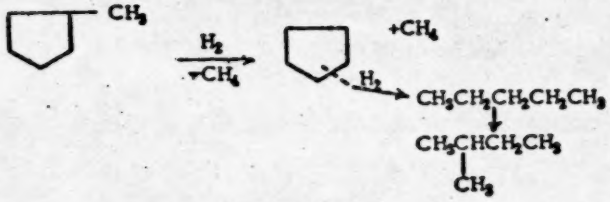
The results of the fractionation of the catalyzate, the analysis of the fractions, and comparison of the properties of the fractions with those of individual hydrocarbons indicate that in the catalytic treatment of benzene under our conditions it undergoes partial hydrogenation to cyclohexane:



which is almost completely isomerized in presence of the catalyst into methylcyclopentane:



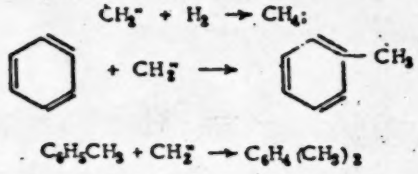
Hydrogenolysis of the methyl group of methylcyclopentane results in the formation of cyclopentane, and part of this is converted into pentane by opening of the ring. The pentane is then partially isomerized to isopentane:



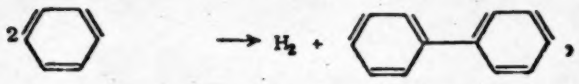
Part of the methylcyclopentane undergoes direct hydrogenolysis at various points in the ring, with formation of hexane isomers.

It is probable that in addition to these reactions there occurs also the breakdown of cycloalkanes, in particular cyclopentane, into methylene radicals

part of which is hydrogenated to methane, the other part being concerned in the methylation of benzene to toluene and xylenes:



These transformations are accompanied by the partial dehydrogenation of benzene, with formation of biphenyl



and also by the synthesis of naphthalene, the mechanism of which cannot at present be explained.

Catalytic Treatment of Toluene

Toluene was passed over the same catalyst under the same conditions, and a yield of 832.8 g (98%) of liquid catalyzate (n_D^{20} 1.4950; d_4^{20} 0.8603) was obtained. As before, 800 g of catalyzate was taken for investigation, and its fractionation was carried out through the same 100-plate column at 740 mm. The results of the analytical fractionation are given in Table 3.

As will be seen from Table 3, the properties of Fractions I and II are close to those for isopentane and pentane [17]. Fraction III (37.5-78.5°) was subjected to chromatographic adsorption, and 1.3 g of naphthenes and paraffins and 1.9 g of benzene were isolated. The naphthene-paraffin part of Fraction III was not investigated in detail owing to the inadequate amount of material available; only its specific gravity (d_4^{20} 0.6973), refractive index (n_D^{20} 1.3970), and aniline point (41.5°) were determined, but these are sufficient to indicate that it contained not only cycloalkanes, but also alkanes, which probably arose by the hydrogenolysis of mono- and di-substituted cyclopentanes.

Fraction IV (78.5-80.1°) and Fraction VI (which boiled constantly at 109.5°), according to their properties, were benzene and unchanged toluene respectively. Fraction VII was submitted to optical investigation, and it was found that, apart from a small amount of toluene, this fraction contained 50% of m-xylene, 30% of p-xylene, and about 20% of o-xylene. The residue from the fractionation of the toluene catalyzate was fractionated at 749 mm

TABLE 3

Fractional Composition of the Benzene Catalyzate

Fraction No.	Boiling range of fraction (°C)	Amount of catalyzate	n_D^{20}	d_4^{20}	Yield (% on amount of catalyzate taken for fractionation)
I	26 - 30.5	1.5	1.3545	0.6203	0.2
II	30.5 - 37.5	3.1	1.3575	0.6258	0.3
III	37.5 - 78.5	3.6	1.4820	0.8003	0.45
IV	78.5 - 80.1	33.9	1.5005	0.8788	4.2
V	80.1 -109.5	0.7	1.4965	–	–
VI	109.5	736.3	1.4960	0.8665	92
VII	109.5 -145	8.6	1.4965	0.8680	1.1
	Residue	5.4	1.5280	–	0.8

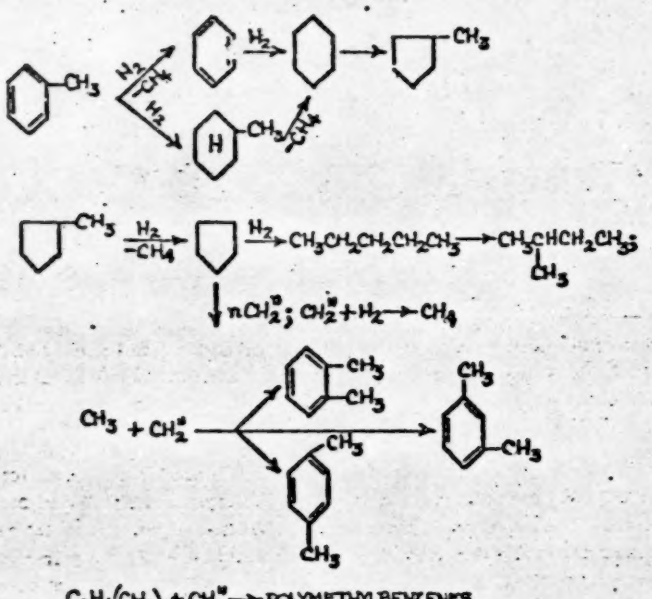
from a Favorskj flask, two fractions being obtained:

Fraction I B. p. up to 200°: 1.3 g; n_D^{20} 1.5085

Fraction II B. p. 200 - 235°: 2.1 g; n_D^{20} 1.5230

The new residue from this distillation solidified when cold to a dark-colored mass, from which it was found possible to sublime some crystals having the odor of naphthalene and melting at 71°.

Fractions I and II (up to 200°, and 200 - 235°) were treated in the cold with alcoholic picric acid. The picrates obtained (0.63 g), which formed golden-orange needles, melted at 148.5°, thus indicating that a small amount of naphthalene was present in these fractions. It would appear that the bulk of the small residue from the fractionation of the toluene catalyzate consisted of a mixture of polyalkylbenzenes, the structures of which could not be established owing to lack of material. The results of the investigation of the separate fractions of the toluene catalyzate provide the basis of the following scheme of the contact-catalysis reactions of this hydrocarbon under the given conditions:



Catalytic Treatment of Ethylbenzene

The catalytic treatment of ethylbenzene under the conditions indicated above yielded 824.5 g (97%) of liquid catalyzate having n_D^{20} 1.4975; d_4^{20} 0.8571. The analytical fractionation of 800 g of this catalyzate was carried out through a column having an efficiency of more than 100 theoretical plates at 750.8 mm. The results are given in Table 4.

TABLE 4

Fractional Composition of the Benzene Catalyzate

Fraction No.	Boiling range of fraction (°C)	Amount of catalyzate, (g)	n_D^{20}	d_4^{20}	Yield (% on amount of catalyzate taken for fractionation
I	26 - 37.5	2.2	1.3560	0.6231	0.25
II	37.5 - 77.5	5.6	1.4725	0.8007	0.7
III	77.5 - 80.5	0.8	1.4940	—	0.1
IV	80.5	116.5	1.5005	0.8769	14.5
V	80.5 - 109.5	2.2	1.4630	0.7859	0.25
VI	109.5 - 110.6	23.6	1.4960	0.8665	2.7
VII	110.6 - 133.5	0.8	1.4960	—	0.1
VIII	133.5 - 136.5	621.8	1.4965	0.8669	77.9
IX	136.5 - 148.0	4.4	1.4965	0.8670	0.5
	Residue	6.1	1.5280	0.8342	0.7

The properties of Fraction I give us reason to suppose that it was a mixture of isopentane and pentane. Benzene was removed from Fraction II by adsorption on silica gel, and the remaining part of the fraction (naphthenes and paraffins; 2.3 g) was analyzed with the aid of Raman spectra. This dearomatized fraction (d_4^{20} 0.6723; n_D^{20} 1.3920; aniline point 64.5°) was found to consist mainly of hexane isomers, including 15% of isohexane. Fraction III (77.5-80.5°) was not investigated owing to lack of material, but Fraction IV (boiling constantly at 80.5°), judging from its properties, was practically pure benzene.

Fraction V (80.5-109.5°) was subjected to chromatographic separation: it consisted of 1.1 g of an aromatic part (a mixture of benzene and toluene) and 1.0 g of a naphthene-paraffin part (n_D^{20} 1.3960 and d_4^{20} 0.7273) consisting, according to its properties, probably of heptane isomers and cycloalkanes. Fraction VI (109.5-110.6) corresponded in properties to pure toluene; Ullmann oxidation of a small part of it yielded benzoic acid, m.p. 121°. The small intermediate Fraction VII (110.6-133.5°) was not investigated. Fraction VIII (133.5-136.5°) was mainly unchanged ethylbenzene. In the oxidation products of a small part of this fraction, only benzoic acid, m.p. 120.8°, was found. Fraction IX (136.5-148°) was subjected to Ullmann oxidation, and from the mixture of acids obtained (3.9 g), 0.3 g of benzoic acid (m.p. 121°), 1.7 g of isophthalic acid, 0.73 g of terephthalic acid, and 0.8 g of phthalic acid were isolated. The isophthalic and terephthalic acids were converted into their methyl esters, which melted at 65.6° and 140° respectively.

The residue (6.1 g) from the fractionation of the catalyzate was separated by fractionation from a Favorsky flask at 758 mm into the following fractions:

Fraction I B. p. 148 - 188°; 2.8 g; n_D^{20} 1.4960; d_4^{20} 0.8743

Fraction II B. p. 188 - 210°; 3.0 g; n_D^{20} 1.5340

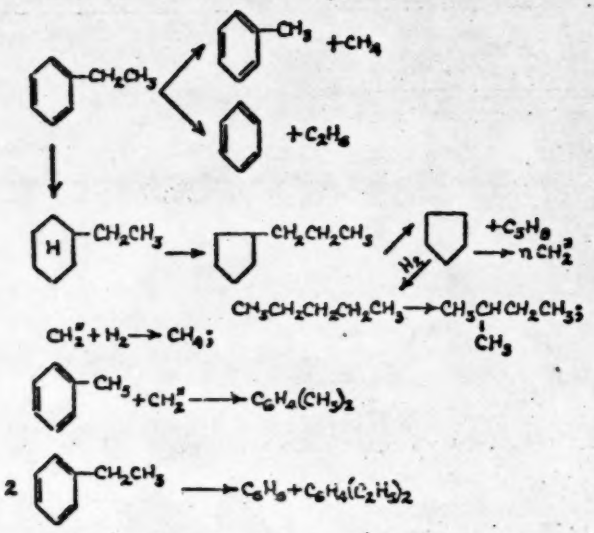
The new residue consisted of a small amount of dark-colored viscous liquid, which was not investigated.

Fraction I (2.8 g) was subjected to Ullmann permanganate oxidation, and it was shown by the methods indicated above that the oxidation products included phthalic, isophthalic, and terephthalic acids. This indicates the presence in the catalyzate of isomeric diethylbenzenes formed, probably, as the result of the displacement of an ethyl group from one ethylbenzene molecule to another. In Fraction II (188-210°) the presence of naphthalene was detected; it was isolated as its picrate, m.p. 149°.

The investigation of the ethylbenzene catalyzate showed that under the given conditions the predominant reaction in the contact-catalysis transformations of ethylbenzene is partial and complete dealkylation to benzene (14.5%) and toluene (2.7%). In addition to this main reaction, the following transformations, which occur to a much less extent, also take place: transfer of an alkyl group from one ethylbenzene molecule to another, hydrogenation of the benzene nucleus and subsequent conversion of the six-membered cycle to a five-membered one, and hydrogenolysis of the latter with formation of the corresponding alkanes, which then undergo isomerization. The gas phase

was analyzed in a Podbielniak apparatus: it consisted of 93% of hydrogen, 4% of propane, and 3% of ethane and methane.

Hence, the composition of the products obtained by the treatment of ethylbenzene in an atmosphere of hydrogen in presence of a platinized alumina catalyst indicates the great variety of the reactions that occur under the given conditions. These reactions probably proceed in accordance with the following scheme:



SUMMARY

1. A study has been made of the contact-catalysis reactions of benzene, toluene, and ethylbenzene at 460° in presence of a platinized alumina catalyst and of hydrogen at a pressure of 20 atm.

2. It has been found that under the conditions used, 3.2% of the benzene, 8% of the toluene, and 22.1% of the ethylbenzene undergo far-reaching changes.

3. It has been established that the transformations of benzene proceed in the directions of hydrogenation to cyclohexane, dehydrogenation to biphenyl, and alkylation with formation of toluene and xylenes. Cyclohexane is isomerized with contraction of the ring into methylcyclopentane, which, in its turn, undergoes hydrogenolysis both in the ring and in the side chain, with formation, respectively, of hexane isomers and cyclopentane; hydrogenolysis of the cyclopentane yields pentane, part of which isomerizes into isopentane.

4. It has been found that the main reaction in the transformation of toluene and ethylbenzene is hydrogenolysis of the side chain with formation of benzene from toluene and a mixture of benzene and toluene from ethylbenzene. In both cases, however, there are simultaneous reactions of hydrogenation of the benzene nucleus, contraction of the six-membered cycle to a five-membered cycle, hydrogenolysis of the latter, and isomerization of the alkanes then formed.

5. In the catalytic treatment of the investigated aromatic hydrocarbons, there were always some products attributable to the methylation of the benzene nucleus by methylene radicals produced by decomposition of the intermediately formed cycloalkanes at the surface of the catalyst.

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N. D. Zelinsky Institute of Organic Chemistry, USSR Academy of Sciences.

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SYNTHESIS OF ESTERS OF POLYVINYL ALCOHOL

S. N. Ushakov and T. A. Kononova

The polymers of vinyl esters – vinyl formate, acetate, propionate, butyrate, etc. – are obtained by the polymerization of the corresponding monomers. In this case the resulting polymers are full esters, and do not contain free hydroxyl groups. In a number of cases, however, both for practical purposes and for the study of the structure and properties of the polymer, it is necessary to synthesize polymers containing definite proportions of hydroxyl groups, i.e. copolymers of vinyl alcohol and the particular vinyl ester. Such copolymers can be obtained only by controlled partial hydrolysis of a polyvinyl ester or by esterification of polyvinyl alcohol (since vinyl alcohol is unknown in the monomeric state and cannot, of course, be used as a component in copolymerization).

In other cases (for example, for the comparative study of the properties of different polymers) it is necessary to obtain polymers having the same average length of chain from esters formed by vinyl alcohol with various acids, and this again cannot be effected by the direct polymerization of the various monomers, owing to the extreme difficulty of preparing polymers that are identical both with respect to the average length of chain and with respect to the statistical distribution of the chain lengths. In this case we can approach the problem only by the careful esterification of polyvinyl alcohol of one given batch with suitable reagents that preclude the degradation of the polymer chains, or by the partial hydrolysis of polyvinyl esters. The study of processes for the esterification of polyvinyl alcohol is therefore of considerable interest. There is much information in the literature on methods of esterifying polyvinyl alcohol. Use is made of the general methods of esterification: treatment of polyvinyl alcohol with acid, anhydrides, or acid chlorides, depending on the nature of the acid residue.

The formylation of polyvinyl alcohol occurs even in absence of catalyst when the polymer is treated with formic acid at room temperature [1]. A single formylation treatment with 100% formic acid results in the formation of an ester containing 70-80 mole-% of ester groups. Complete esterification of polyvinyl alcohol is obtained by four treatments with 100% formic acid, and no chain degradation occurs. When the temperature is raised to 60° or higher, highly substituted esters are obtained immediately, but the process is accompanied by degradation of the main chain of the polyvinyl alcohol. The use of catalysts (surfuric acid, zinc chloride) leads to a reduction of the degree of substitution by formyl groups owing to partial dehydration of the polyvinyl alcohol.

The acetylation of polyvinyl alcohol has been studied by many investigators [2, 3, 4]. For acetylation it is necessary to use acetic anhydride. It may be carried out by the action of acetic anhydride on polyvinyl alcohol in pyridine [5, 6]: when polyvinyl alcohol was heated in a water bath for 24 hours with ten parts of a mixture of two parts of acetic anhydride and one part of pyridine, a polyvinyl acetate having a degree of substitution of 80 mole-% was obtained. Completely acetylated polyvinyl alcohol was obtained when polyvinyl alcohol prepared by alkaline hydrolysis was heated at 60° with a mixture of pyridine and acetic anhydride in an atmosphere of nitrogen for 20 days; the average degree of polymerization remained unchanged in this process.

Complete acetylation of polyvinyl alcohol has been effected also by the action of a mixture of acetic anhydride and acetic acid on polyvinyl alcohol pretreated by swelling in water, removal of water by suction, and dehydration with alcohol and ether [7].

Of the esters formed by polyvinyl alcohol with unsaturated monobasic acids, the methacrylic ester is known: it was prepared by the action of methacryloyl chloride on polyvinyl alcohol in absence of solvent. Also, by the action of methacrylic acid in benzene, esterification proceeded to the extent of 12-14 mole-%, and the products were insoluble in organic solvents. In this case a cross-linked polymer was formed by the participation of the double bonds of the methacrylic acid residues.

Esters of polyvinyl alcohol with dibasic acids – adipic, maleic, sebacic, and succinic – have been obtained [8] by reaction of polyvinyl alcohol with the anhydrides and acid chlorides. In the case of succinic acid only acid esters were obtained, which was confirmed by direct titration and by methylation of the carboxyls. Sebacic acid yielded full esters, and cross linking of the polyvinyl alcohol chains occurred with formation of a three-dimensional polymer.

Some polyvinyl esters, and also mixed esters, have been obtained by reaction of polyvinyl acetate with anhydrides of di- and poly-carboxylic acids in presence of water and a suitable solvent. In this way the preparation has been effected of the polyvinyl esters of succinic, glutaric, maleic, and phthalic acids, and also mixed esters of these

acids [9]. When polyvinyl alcohol is esterified with citric, tartaric, maleic, and lactic acids, water-soluble derivatives are obtained, which can be used as thickening agents in the textile industry. Among the inorganic esters of polyvinyl alcohol, the nitrate and sulfate have been studied.

Several methods have been proposed for the preparation of polyvinyl nitrate [10]; they include a) treatment of a solution of polyvinyl alcohol in sulfuric acid with nitric acid; b) direct nitration with nitric acid in an atmosphere of an inert gas; c) nitration with a mixture of sulfuric and nitric acids at below 0° [11]. The sulfuric ester of polyvinyl alcohol may be obtained by treatment of polyvinyl alcohol in pyridine with chlorosulfonic acid [12].

Our investigation aimed at the development and improvement of methods for the preparation of a number of esters of polyvinyl alcohol (polyvinyl formate, acetate, propionate, butyrate, and isobutyrate) containing various portions of free hydroxyl groups and having the same average chain length and polydispersity. As indicated above, methods for the synthesis of the formate and acetate from polyvinyl alcohol have been described in the literature, but not in relation to our present objects. There is no information in the literature about polyvinyl propionate, butyrate, and isobutyrate.

EXPERIMENTAL

The starting material was polyvinyl alcohol having an acetyl content of 1.8 mole-%. It was prepared by the alkaline alcoholysis of polyvinyl acetate in methanol and had an intrinsic viscosity of $[\eta] = 0.74$ (after reprecipitation). The whole of the work was carried out with polyvinyl alcohol that had not been reprecipitated, the fact that a partial fractionation occurs in the precipitation of our polyvinyl esters and the products of their hydrolysis being taken into account. For this reason, all comparisons of the intrinsic viscosities of polyvinyl alcohols obtained by the hydrolysis of the esters were made with the intrinsic viscosity of the reprecipitated original polyvinyl alcohol, which (in spite of some difference in the conditions of reprecipitation) gives a truer characterization of the variation of $[\eta]$ in the process of esterification and hydrolysis.

We have studied the following esters of polyvinyl alcohol: 1) the formate, 2) the acetate, 3) the propionate, 4) the butyrate, and 5) the isobutyrate. The degree of substitution by ester groups was varied from 100% to 30% (to 10% in the case of the formic ester).

For the preparation of the completely substituted formic ester, 100% formic acid was used, and for the preparation of formic esters having a low degree of substitution, aqueous formic acid at various concentrations was used. The full esters of the other acids were prepared by the action of the corresponding anhydrides on polyvinyl alcohol in pyridine at 80-95°. For the acetylation, chemically pure acetic anhydride was used, and it was vacuum-distilled before the experiment. The partially substituted esters of the homologs of formic acid were obtained by alcoholysis of the fully substituted esters. After the esterification and alcoholysis the esters were obtained as solutions, from which they were precipitated by addition to a suitable nonsolvent.

The polymers were purified by reprecipitation, and were then carefully washed and dried by the methods indicated below. The precipitation of polyvinyl formates was effected by pouring the polymer solution in a thin stream into the nonsolvent with stirring. The precipitation of the acetic, propionic, butyric, and isobutyric esters was carried out as follows. Several drops of the polymer solution were placed on the surface of water in a crystallizing dish, and they then spread over the surface and formed a thin film. The film remained for some time on the surface of the water, and the solvent diffused from it into the water. The film was then transferred to a beaker of clean water. The large surface of the precipitated polymer facilitated its thorough washing. Two precipitations of the polymer purified it completely from pyridine and acids, a result that could not be obtained by the usual method of precipitation, i.e. the pouring of the polymer solution in a thin stream into water with stirring.

Polyvinyl formates were dried in a vacuum drier at room temperature and a residual pressure of 10 mm Hg. The acetic propionic, butyric, and isobutyric acids were dried over calcium chloride at a residual pressure of 5-10 mm Hg. When the content of ester groups was not below 90-80 mole-%, the temperature of drying was about 40°; for lower contents of ester groups the esters were dried at room temperature. Polyvinyl acetates having acetyl contents of not less than 90 mole-% were given a porous structure before they were dried; this effect we obtained by the sublimation of benzene from a solution of the polymer [13].

Polyvinyl acetates having acetyl contents of 70-45 mole-% were insoluble in benzene and formed a compact mass when vacuum-dried. It was practically impossible to remove water from this mass, and the esters were therefore dried by means of high-frequency currents, a 1-kw laboratory apparatus working at a wavelength of 5 μ and a frequency of $5.4 \cdot 10^7$ cycles per second being used.

The content of ester groups in the polyvinyl esters was determined by hydrolysis of a weighed amount of ester (0.2-0.4 g) with alkali at the boil for eight hours, the excess of alkali being titrated to phenolphthalein with 0.1 N HCl. The alkali used was 0.1 N aqueous NaOH in the case of polyvinyl formate, and 0.1 N alcoholic KOH in the case of polyvinyl acetate, propionate, butyrate, and isobutyrate.

Polyvinyl Formates. The fully substituted formic ester of polyvinyl alcohol was prepared by a previously described method [1]. A weighed amount of polyvinyl alcohol was covered with six times the weight of 100% formic acid and set aside at room temperature (16-18°) for 50 hours. In the course of this time the whole of the polyvinyl alcohol passed into solution. The solution was then diluted with acetone so as to bring the concentration of ester in the solution to 5-6%, and the polymer was precipitated by pouring the solution gradually into ethanol. It was then carefully washed with alcohol until neutral, and vacuum-dried (10-12 mm Hg) at room temperature. In order to attain 100% substitution, the formylation was performed four times successively (Table 1).

TABLE 1

Content of Formate Groups in the Ester after Successive Formylations

	Content of formate groups		Solvent
	% by weight	mole-%	
Formylation I	57	86.0	Acetone, pyridine
Formylation II	60	93.6	Dioxane, chloroform
Formylation III	61.2	96.6	Dioxane, chloroform
Formylation IV	62.2	99.2	Dioxane, chloroform

Formic esters having contents of ester groups of less than 80 mole-% have not been described in the literature. We have prepared such esters by the formylation of polyvinyl alcohol both by 100% formic acid and also by diluted acid, the temperature of the reaction and its duration being varied according to the degree of esterification required. The results of the experiments are given in Table 2. Polyvinyl formates having a degree of substitution of more than 70 mole-% were precipitated from acetone by means of methanol or ethanol (the polyvinyl formate having a degree of substitution of 10% was precipitated from the reaction mixture by means of methanol), when they formed threads, which were converted into white opaque pieces when vaccum-dried for 50-70 hours. For degrees of substitution of 68-36 mole-%, the reaction mixture was precipitated in alcohol as a slimy material, which was carefully and repeatedly washed with alcohol until neutral, and then finally washed with ether. The polymer was then placed on glass in the form of a thin layer and was vacuum-dried at room temperature. In spite of the fact that the films acquired a porous structure owing to the rapid evaporation of the ether, drying to constant weight lasted for 150-200 hours.

The fully substituted polyvinyl formate obtained from polyvinyl alcohol was hydrolyzed to polyvinyl alcohol by treatment at the boil for six hours with 5% aqueous formic acid. For the polyvinyl alcohol so obtained the intrinsic viscosity was determined graphically ($[\eta] = 0.77$).

TABLE 2

Dependence of the Content of Formate Groups in Esterified Polyvinyl Alcohol on the Concentration of the Esterifying Formic Acid, on the Temperature, and on the Duration of the Reaction

Concentration of formic acid (%)	Bath ratio	Reaction temperature (°C)	Duration of reaction (hours)	Content of formate groups		Solvent used for the production of the film
				% by weight	mole-%	
100	1:6	18	24	53.3	78.0	Acetone
78	1:10	18	30	49.6	68.7	80 % aqueous acetone
100	1:6	18	4	41.0	53.8	75 % aqueous acetone
78	1:10	0	15	37.7	48.1	85 % aqueous acetone
78	1:10	-2	6	30.0	36.3	50 % aqueous acetone
35*	1:20	18	2	10.0	10.4	

Polyvinyl Acetate. The acetic ester of polyvinyl alcohol was prepared by the esterification of polyvinyl alcohol with acetic anhydride in a pyridine medium. The reaction was carried out as follows: polyvinyl alcohol (4 g) was covered with pyridine (35 ml), and the mixture was set aside at room temperature for twelve hours. Acetic

* In this case the polyvinyl alcohol was first dissolved in water, and then formic acid was added to the 70% aqueous solution in such amount that its concentration in the solution was 35%.

anhydride (30 ml) was then added, and the mixture was heated in a boiling water bath. After 30 minutes the polymer has swollen so much that the stirrer could no longer operate in the reaction mixture. After one hour the whole of the polymer had gone into solution. After three hours from the beginning of the reaction the mixture was cooled and diluted with 50 ml of acetone; the mixture was quite colorless. The polymer was precipitated from solution in a large amount of water; it was carefully washed free from reaction products and then dried. It was then again precipitated from an acetone solution into water. Before being dried for analysis the polymer was given a porous structure by the sublimation of benzene from a solution of the polymer. The content of ester groups in the ester so obtained was 96.5 mole-%. In order to check for the absence of chain degradation in the course of the reaction, the polyvinyl acetate was saponified to polyvinyl alcohol by alcoholysis in absolute methanol containing 0.4% of KOH. The intrinsic viscosity of the polyvinyl alcohol so obtained was determined ([η] = 0.72).

In order to obtain partially substituted polyvinyl acetates, the polyvinyl acetate from which the polyvinyl alcohol used in this work was prepared was subjected to saponification, which was carried out in absolute methanol at a bath ratio of 1:6 with various amounts of KOH for 13-15 hours at room temperature. After 13-15 hours the reaction mixture was diluted with acetone (Expt. No. 1 and 2, Table 3) or aqueous acetone (Expt. No. 3 and 4), and the polymer was precipitated in water. The polymers from Expt. No. 2, 3, and 4 precipitated in the form of slimy material, and when they were air-dried a crust formed on their surfaces which prevented further drying. These polymers, therefore, were first dried with the aid of high-frequency currents and then under a reduced pressure of 10 mm Hg at 20-25°. The vacuum drying was continued for 50-70 hours.

Polyvinyl Propionate. As indicated above, propionic esters of polyvinyl alcohol have not been described in the literature. We have prepared the fully substituted propionic ester of polyvinyl alcohol by the esterification of polyvinyl alcohol with propionic anhydride in pyridine. The reaction was carried out as follows: polyvinyl alcohol (4 g) was covered with pyridine (30 ml), and the mixture was set aside at room temperature for twelve hours. The mixture was then stirred, and propionic anhydride (15 ml, i.e. 1.25 mole per mole of polyvinyl alcohol) was added. The mixture was heated in a boiling water bath, and after one hour the polyvinyl alcohol had swollen to such and extent that the stirrer could no longer operate in the reaction mixture. After 90 minutes the mixture had become thinner, and after three hours the whole of the polymer had passed into solution. After five hours from the beginning of the reaction, heating was discontinued, the solution was cooled, and 60 ml of acetone was added. The solution was yellow. The polymer was precipitated from solution in a large amount of water; it was then carefully washed with water and dried for 30 hours at 10 mm Hg and at 45°. It was then reprecipitated, carefully washed, and dried under the same conditions to constant weight (50 hours). The content of ester groups was 72.5% by weight, or 98.5 mole-%.

TABLE 3

Saponification Conditions, and the Properties of Polyvinyl Acetates

Expt. No.	Amount of KOH (%)	Duration (hours)	Form of reaction mixture	Diluent	Content of acetate groups in polymer	
					% by weight	mole-%
1	0.05	14	Liquid	Acetone	58.0	70.8
2	0.15	14	Liquid	Acetone	54.3	66.0
3	0.25	15	Gel	66% Aqueous acetone	50.4	58.5
4	0.32	15	Gel	50% Aqueous acetone	43.4	45.5

Propionic esters of polyvinyl alcohol having various contents of ester groups were obtained by saponification of the 98.5% ester in absolute methanol by means of various amounts of KOH at room temperature (Table 4). The reaction mixture was poured into water, and the product was carefully washed with water for 48 hours and dried at room temperature at a residual pressure of 10 mm Hg. The saponification of the polyvinyl propionate obtained to polyvinyl alcohol was carried out with 1% KOH in absolute methanol. The intrinsic viscosity of the polyvinyl alcohol obtained was [η] = 0.77.

Polyvinyl Butyrate. Butyric esters of polyvinyl alcohol have not been described in the literature. We have prepared the fully substituted butyric ester of polyvinyl alcohol by the esterification of polyvinyl alcohol with butyric anhydride in pyridine. The reaction was carried out in a similar way to that for polyvinyl propionate. Before precipitation of the polymer, the reaction mixture was diluted with methanol. The polymer was precipitated in water, but the films stuck together when washed with water in the beaker. After being washed for 48 hours, the polymer was dried in a vacuum drier at 40° and 10 mm Hg for ten hours. It was then dissolved in ethanol and precipitated in water; this time the films did not stick together during washing. Drying to constant weight was carried out in a vacuum drier at 40° and 10 mm Hg. The product was a compact piece of light-brown rubberlike polymer having an ester-group content of 99.95 mole-%.

TABLE 4

Saponification Conditions, and the Properties of Polyvinyl Propionates

Expt. No.	Amount of KOH (%)	Duration (hours)	Form of reaction mixture	Diluent	Content of ester groups	
					% by weight	mole-%
1	0.2	13	Liquid	Acetone	62.5	72.6
2	0.3	16	"	"	52.8	53.4
3	0.4	14	Gel	50% Aqueous acetone	40.0	34.7
4	1.0	24	"	Water	2.0	1.2

Butyric esters of polyvinyl alcohol containing various proportions of ester groups were obtained by the saponification of the 100% ester in absolute methanol at room temperature with various amounts of KOH (Table 5, Expt. No. 1, 2, and 3).

The esters obtained were precipitated in water, carefully washed with water for 48 hours, and dried at room temperature at a residual pressure of 10 mm Hg. The intrinsic viscosity of the polyvinyl alcohol obtained from polyvinyl buyrate by saponification was $[\eta] = 0.78$.

TABLE 5

Saponification Conditions, and the Properties of Polyvinyl Butyrates

Expt. No.	Amount of KOH (%)	Duration (hours)	Form of reaction mixture	Diluent	Content of ester groups	
					% by weight	mole-%
1	0.5	14	Liquid	Acetone	68.3	76.4
2	0.6	14	"	Methanol	64.2	67.0
3	1.0	12	Gel	50% Aqueous ethanol	43.5	35.4
4	2.0	15	"	Water	2.0	1.0

Polyvinyl Isobutyrate. Isobutyric esters of polyvinyl alcohol have not been described in the literature. We have prepared an almost fully substituted isobutyric ester of polyvinyl alcohol by the esterification of polyvinyl alcohol with isobutyric anhydride in pyridine. The course of the reaction was similar to that of butyric anhydride; it was complete in nine hours. The content of ester groups in the product was 75.3% by weight, or 96.7 mole-%. Isobutyric esters of polyvinyl alcohol having different proportions of ester groups were prepared by the saponification of the 96.7% ester in absolute methanol at room temperature with various amounts of KOH (Table 6, Expt. No. 1, 2, and 3).

TABLE 6

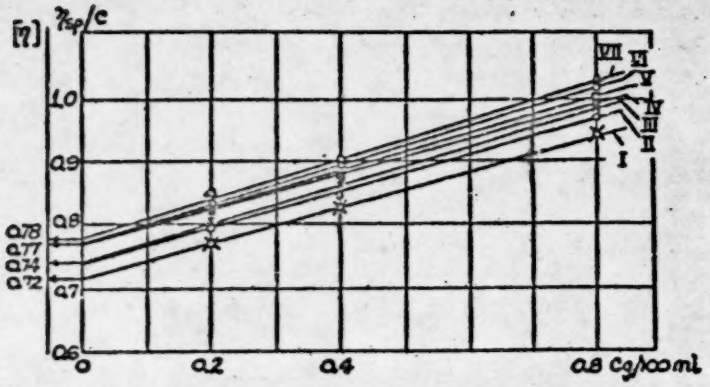
Saponification Conditions, and the Properties of Polyvinyl Isobutyrate

Expt. No.	Amount of KOH (%)	Duration (hours)	Form of reaction mixture	Diluent	Content of ester groups	
					% by weight	mole-%
1	0.75	14	Liquid	Ethanol	68.5	77.70
2	1.0	18	Viscous liquid	50% Aqueous ethanol	58.5	56.0
3	2.0	20	Gel	80% Aqueous methanol	44.3	34.7
4	4.0	48	"	Water	2.4	1.4

The esters obtained were precipitated in water, carefully washed with water for 48 hours, and dried at room temperature at a residual pressure of 10 mm Hg.

Polyvinyl alcohol obtained from polyvinyl isobutyrate had an intrinsic viscosity of $[\eta] = 0.73$.

The dependence of η_{sp}/C on C for polyvinyl alcohols obtained from various esters is shown graphically in the figure.



Dependence of η_{sp}/C on C for polyvinyl alcohols obtained from various esters: 1 - from polyvinyl acetate; 2 - from polyvinyl isobutyrate; 3 - the original reprecipitated sample; 4 - from polyvinyl formate; 5 - from polyvinyl propionate; 6 - from polyvinyl formate; 7 - from polyvinyl butyrate

SUMMARY

1. The syntheses have been effected of esters of polyvinyl alcohol with the following acids: formic, acetic, propionic, butyric, and isobutyric (the last three have not been described previously). The degree of substitution varied from 100 to 30 mole-% (to 10 mole-% in the case of polyvinyl formate).

2. The preparation of these polyvinyl esters was accompanied by the maintenance of the mean length of the macromolecular chains within comparable limits. This was shown by saponifying the esters to polyvinyl alcohol and comparing the intrinsic viscosities of the products with that of the polyvinyl alcohol from which the esters were prepared. The intrinsic viscosities of the polyvinyl alcohols obtained from the various polymers varied within the limits $[\eta] = 0.72\text{-}0.78$, while the intrinsic viscosity of the original (reprecipitated) polyvinyl alcohol was 0.74.

3. Various methods were used for the preparation of these esters of polyvinyl alcohol. Formic esters of polyvinyl alcohol having various degrees of substitution were synthesized by treatment of the polyvinyl alcohol with formic acid of various concentrations. For the preparation of almost fully substituted acetic, propionic, butyric, and isobutyric esters, the general method of esterification was used in which the polyvinyl alcohol is treated with the anhydride of the corresponding acid in a pyridine medium. Partial esters were obtained by partial alcoholysis of the full esters in methanol containing KOH at various concentrations.

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Lensoviet Leningrad Institute of Technology

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COMMUNICATION 4. COPOLYMERIZATION OF SOME VINYL COMPOUNDS WITH 2-VINYLOXYETHANOL

M. F. Shostakovsky and A. M. Khomutov

Investigations of polymerization and copolymerization reactions of vinyl ethers and acrylic acid derivatives have shown that the formation of polymers and copolymers by a free-radical mechanism is in principle possible [1, 2, 3]. In the course of these studies the laws governing these reactions, and also the nature of the initiator, have been revealed. An important factor in the effecting of this reaction is the choice of initiator [4]. An essential condition with respect to the nature of the radical is that its free valency must not belong to oxygen. These considerations apply mainly to the initiation of the reaction of vinyl ethers by the free-radical mechanism, and they are probably of great importance in other cases also. The course of polymerization and copolymerization depends on the reactivities of the monomers, which are determined not only by the double bonds, but also by the presence, for example, of the mobile hydrogen of hydroxyl groups, etc.

A defect of earlier investigations has been that the decomposition of, for example, benzoyl peroxide has been treated in an extremely schematic manner and only the reaction of double bonds has been taken into consideration. The investigations in this field, however, show that these reactions have many aspects and are accompanied by a number of side reactions, which have been established by us by a study of the reaction products, and which confirm the complicated mutual effects of atoms in the molecule that were predicted by the great Russian chemist Markovnikov [5].

In the present investigations we have examined the copolymerization of 2-vinyloxyethanol with methacrylic acid, with methyl methacrylate, and with styrene.

2-Vinyloxyethanol [6] $OHCH_2CH_2OCH = CH_2$ contains clearly defined reaction centers: the double bond, the oxonium oxygen, and the hydroxyl with the mobile hydrogen. Such a structure confers a number of peculiar properties on the substance. Thus, 2-vinyloxyethanol readily isomerizes, and under the usual conditions exists in the associated state [7]:

$$CH_2 = CHOCH_2CH_2OH \rightarrow CH_3CH\begin{matrix}OCH_2\\ |\\ OCH_2\end{matrix}$$

Accordingly, 2-vinyloxyethanol does not polymerize under the influence of metal chlorides and acids [8].

On the basis of these properties of 2-vinyloxyethanol, it would be expected that, in reacting with methacrylic acid or methyl methacrylate, copolymerization would occur with participation of the double bonds, and that reactions would occur in which the functional groups would take part.

As indicated above, as copolymerization components we used methacrylic acid, methyl methacrylate, and styrene. These vinyl compounds have a number of chemical peculiarities. Thus, methacrylic acid gives "acylals" with vinyl ethers; methyl methacrylate is capable of undergoing alcoholysis [9]:

$$CH_2 = \overset{CH_3}{\overset{|}{C}} - COOCH_3 + ROH \rightarrow CH_2 = \overset{CH_3}{\overset{|}{C}}OOR + CH_3OH$$

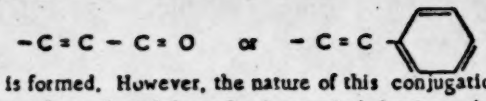
Styrene has a very reactive double bond [9]; its phenyl group is not reactive. Styrene has a structure in which a double bond is conjugated with a benzene nucleus:

$$CH_2 = \overset{H}{\overset{|}{C}}$$

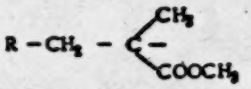
Our investigations show that 2-vinyloxyethanol copolymerizes with methacrylic acid and with methyl methacrylate, but not with styrene.

From this we may assume that, when the free radical of the initiator reacts with a molecule containing a

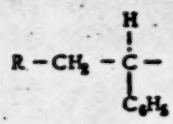
conjugated bond system



a complex radical is formed. However, the nature of this conjugation has a marked effect on the nature of the more complex radical formed, and the radicals vary in behavior; thus the radical



is more active than the radical

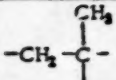
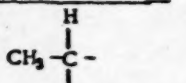


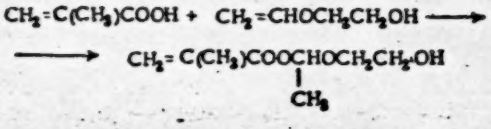
Our study of the interaction of methacrylic acid and 2-vinyloxyethanol has shown that the formation of copolymers occurs. Increase in the amount of 2-vinyloxyethanol in the reaction medium results in a reduction in yield of copolymer and an increase in the proportion of vinyloxyethanol residues in the chain (Table 1). Similar behavior has been observed for other vinyl ethers [1].

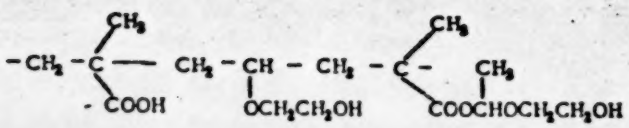
In the analysis of the copolymers, not only carboxyl groups, but also acetaldehyde was found, thus indicating the presence of "acylals", which could be formed during the reaction as indicated in the following schemes:

TABLE 1

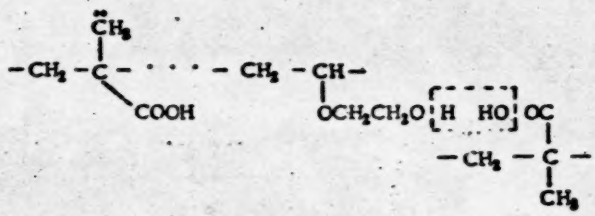
Yields and Compositions of Copolymers of Methacrylic Acid and 2-Vinyloxyethanol

No.	Molar ratio (%)		Yield (%)	Analysis of copolymer		Composition of copolymer (%)	
	$CH_2=C(CH_3)COOH$	$CH_2=CHOCH_2CH_2OH$		meth-acrylic acid (%)	2-vinyl-oxyethan-ol (%)		
1	100	–	91.5	99.5	–	100	–
2	95	5	78.63	96.75	3.25	96.82	3.18
3	75	25	71.07	88.58	11.42	88.82	11.18
4	50	50	57.35	74.66	25.34	75.05	24.95
5	25	75	41.24	66.2	34.8	66.85	33.15
6	5	95	13.14	40.85	59.15	41.64	58.36
7	–	100	Nil	–	–	–	–

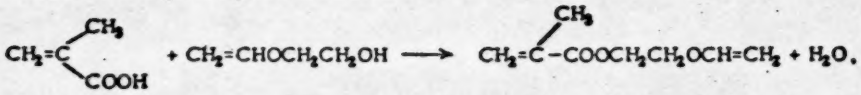




Unlike previously described [3] copolymers of methacrylic acid and vinyl ethers, those obtained from the pairs of monomers used in this investigation are insoluble substances that swell in the usual solvents. It may be pointed out here that cross-linking of the macromolecules is observed for equimolecular proportions of monomers, or when there is an excess of 2-vinyloxyethanol. Since vinyl ethers that do not contain a hydroxyl group do not give cross-linking, the occurrence of the phenomenon in the present case must be attributed to the hydroxyl of 2-vinyloxyethanol.

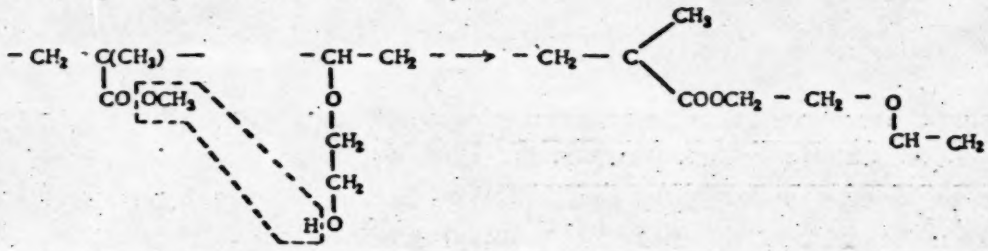


or first of all a divinyl compound is formed:

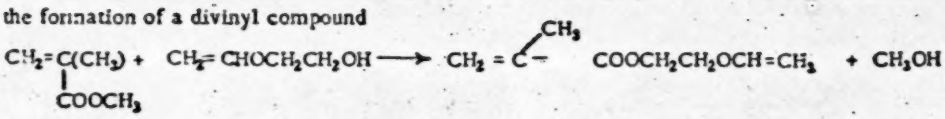


which then takes part in the copolymerization reaction.

We will pass to a discussion of the copolymerization of the other member of the acrylic series, methyl methacrylate, with 2-vinyloxyethanol. In this case also, with increase in the concentration of 2-vinyloxyethanol the yield of copolymer falls and the proportion of 2-vinyloxyethanol residues in the chain rises. When the proportion of 2-vinyloxyethanol in the reaction mixture exceeds 50 mole-%, the formation of a three-dimensional polymer is observed, which is probably to be attributed to alcoholysis:



or the formation of a divinyl compound



which then takes part in the copolymerization reaction. In the same medium, simultaneously with the three-dimensional polymers, copolymers of good solubility in acetone are formed. These, however, do not correspond in composition to a polymer of methyl methacrylate (Table 2). Since these two monomers have almost the same carbon contents, the compositions of the copolymers were determined by analysis for functional groups (Table 2).

Experiments on the copolymerization of styrene and 2-vinyloxyethanol did not yield positive results: in all cases polystyrene was isolated (Table 3).

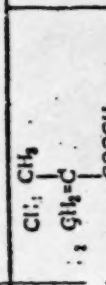
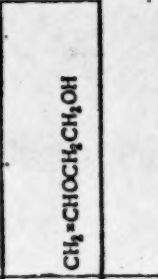
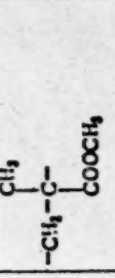
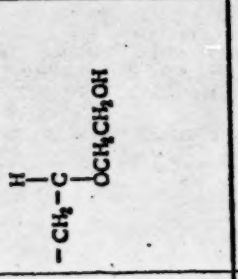
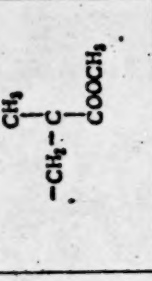
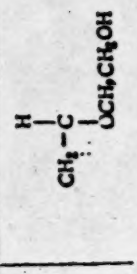
EXPERIMENTAL

The monomers used in this investigation were freshly distilled, and their constants were as follows. Methacrylic acid: b.p. 160°; n_D^{20} 1.4313; d_4^{20} 1.0153; acid number 650 ml of KOH. Methyl methacrylate: b. p. 100.5°; n_D^{20} 1.4150; d_4^{20} 0.936. Styrene: b.p. 146°; n_D^{20} 1.5420; d_4^{20} 0.9072.

2-Vinyloxyethanol: b.p. 140°; n_D^{20} 1.4368; d_4^{20} 0.9805. Methanol: b. p. 64-65°; n_D^{20} 1.3300. Benzene: b. p. 80-80.5°; n_D^{20} 1.5010. Acetone: b. p. 56°; n_D^{20} 1.3595.

TABLE 2

Yields and Compositions of Copolymers of Methyl Methacrylate and 2-Vinyloxyethanol

No.	Molar ratio (%)		Yield	Ratio of monomer units in copolymer by analysis (%)		Composition of copolymer (mole-%)	
							
1	100	—	97.00	100	—		
2	95	5	88.2	85.7	14.3	84.06	15.94
3	75	25	70.12	83.17	16.83	81.3	18.7
4	55	50	62.00	56.0	44.0*	50.66	79.34
5	25	75	29.00	51.39	48.61	48.20	51.8
6	5	95	10.23	33.9	66.1	31.10	68.90
7	—	100	Nil	—	—	—	—

* Composition of the copolymer as calculated from elementary analysis for C and H: methyl methacrylate residues 56.9%, 2-vinyloxyethanol units 43.1 mole %.

TABLE 3

Yields and Compositions of Polymers

No.	Molar ratio (%)		Yield (%)	%C	%H
	$CH_2=CHC_6H_5$	$CH_2=CHOCH_2CH_2OH$			
1	100	—	91.0	92.2	
2	75	25	58.6	92.52	7.66
				92.40	7.85
3	50	50	51.46	92.15	7.73
				92.15	7.87
4	25	75	18.59	92.19	8.07
				91.95	7.99

Experimental Procedure

The copolymerization was carried out in sealed glass tubes at 60 ± 1°. The total amount of the starting materials, which were taken in various proportions, was 10 g, and 0.2% of benzoyl peroxide on the total weight of monomers was added. The process proceeded continuously for 100 hours, when solid or highly viscous products were obtained. Control experiments on the polymerization of the separate monomers were carried out in presence of benzoyl peroxide under the same conditions. When the process was complete, the tubes were cooled to 0°. The reaction products were purified by bringing them into solution and then reprecipitating them. In those cases in which no reaction could be established by the formation of precipitates, the contents of the tube were fractionally distilled.

When polymers were present, dissolution and reprecipitation were repeated until removal of the original monomers was complete. The macromolecular products were then dried to constant weight. The compositions of the copolymers were then determined. The solutions obtained after precipitation and dissolution were vacuum-factionated in a system having cooled traps. The residue in the distillation flask was dried to constant weight. The amounts of the original monomers in the distillates were determined. On the basis of the results so obtained the compositions of the copolymers were calculated and the general balance sheet of the reaction products was made out. We give here the most characteristic results from numerous investigations of copolymerization.

1. Copolymerization of methacrylic acid and 2-vinyloxyethanol

The amounts taken for the copolymerization were 5 g of methacrylic acid and 5 g of 2-vinyloxyethanol (molar ratio 1:1). The conditions of the copolymerization and the method of isolating the copolymers are described above. The resulting copolymer was a swollen gel, insoluble in methanol; it was treated with ether until there were no longer reactions for double bonds and carboxyl groups. Since the carbon contents of the original monomers were not greatly different – 55.8% for methacrylic acid and 54.54% for 2-vinyloxyethanol – the determination of the elementary composition served no purpose in this case. The compositions of the copolymers were therefore established by carboxyl estimations (in the control sample of methacrylic acid polymer, 99-100% of the carboxyl content was accounted for by titration).

The materials isolated as a result of these investigations were: a) 5.7346 g of copolymer; b) 3.8178 g of material remaining in the distillation flask after the fractionation; c) 0.1 g of methacrylic acid and 0.12 g of 2-vinyloxyethanol, which were determined by titration of a mixture of solvent and precipitant. The total amount accounted for was 9.74 g, which is 97.4% of the weight of the monomers taken for reaction.

Analysis of the copolymer showed that it contained 57.8% of carboxyl groups, which corresponds to the same percentage content of methacrylic acid. The residue in the distillation flask was also analyzed for carboxyl content, and acetaldehyde was determined titrimetrically (by the iodometric method). It was found that carboxyl groups and acetaldehyde were present.

The copolymerization of these monomers was studied also for other molar ratios. When reaction was complete, the products were treated under the conditions of the above-described experiment. The results of the investigation of these copolymers are given in Table 1.

Thus, the copolymers contained methacrylic acid and 2-vinyloxyethanol units and acylal groupings.

2. Copolymerization of $CH_2=C(CH_3)COOCH_3$ and $CH_2=CHOCH_2CH_2OH$ (molar ratio 1:1)

The amounts taken for the copolymerization were 2.65 g of methyl methacrylate and 2.35 g of 2-vinyloxyethanol. The conditions of the copolymerization and the method of purifying the copolymers are described above. The copolymer was not completely soluble in acetone; the solution contained a swollen gel, which was treated with acetone and then ether until there was no longer a reaction for double bonds. The copolymer gel was dried, and the yield was found to be 2.67 g. The solution (0.5 ml) obtained after the separation and purification of the copolymer gave no precipitate with methanol. It gave a precipitate with water, however, and the whole of the solution was therefore slowly poured into water. The resulting precipitate was washed until there was no longer a reaction for a double bond, and was then dried and weighed (0.43 g).

Two products were therefore isolated. Elementary analysis showed that they contained 57.78% C (gel) and 58.30% C (soluble copolymer). As the carbon contents of the original monomers differed by only 5.5%, the compositions of the copolymers were established by estimation of the 2-vinyloxyethanol hydroxyl groups. Methyl methacrylate was determined by titration in the solutions remaining after separation of the copolymers.

After distillation of this solution, followed by drying under reduced pressure, 1.63 g of liquid remained in the distillation flask; this was found to be a mixture of the original monomers and products of their reaction. Hence, from the original 5 g of monomers, 4.83 g of products were isolated.

The copolymerization of these monomers was studied also for other molar ratios. When reaction was complete, the products were treated under the conditions of the previous experiments. The results of the investigation of these copolymers are given in Table 2.

It may be pointed out that, when the reaction was carried out at a molar ratio of 1:3 ($CH_2=C(CH_3)COOCH_3$ and $CH_2=CHOCH_2CH_2OH$), the resulting copolymers were insoluble in acetone, but when the inverse ratio was used (3:1) the copolymers dissolved readily in acetone.

3. Interaction of $CH_2=CHC_6H_5$ and $CH_2=CHOCH_2CH_2OH$

These monomers were investigated at various molar ratios. The polymerization conditions are described above. The resulting polymers were treated with methanol until there was no longer a reaction for double bonds. They were then dried and analyzed for C and H contents. Results for several ratios are given in Table 3, from which it will be seen that in all of these experiments pure polystyrene was isolated, i.e. no copolymerization occurred.

SUMMARY

1. Copolymers of 2-vinyloxyethanol with methacrylic acid and with methyl methacrylate have been prepared.

2. It has been shown that increase in the proportion of 2-vinyloxyethanol in the reaction mixture results in lower yields of copolymers and in the formation of three-dimensional copolymers.

3. It has been shown that styrene does not form copolymers with 2-vinyloxyethanol in presence of benzoyl peroxide.

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N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

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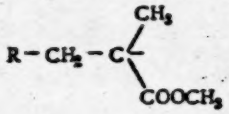
**** " " " " p. 1243.

REACTIONS OF UNSATURATED AND MACROMOLECULAR COMPOUNDS

COMMUNICATION 5. COPOLYMERIZATION OF METHYL ACRYLATE WITH VINYL ETHERS

M. F. Shostakovsky and A. M. Khomutov

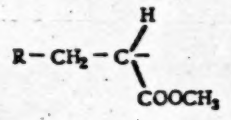
Investigations of the polymerization and copolymerization reactions of methacrylic acid, methyl methacrylate, and various vinyl ethers have resulted in a considerable extension of our ideas in this field [1, 2, 3]. For example, these investigations have established the importance of the nature of the radicals present, particularly those formed by the decomposition of benzoyl peroxide. These radicals are unable to initiate the polymerization of vinyl ethers, and we consider that their ineffectiveness is to be explained by the fact that in these radicals the free valency is on oxygen. Radicals having free valencies on C, N, S, and other elements have initiating properties also for the reactions of vinyl ethers. As regards the part played by benzoyl peroxide and the radicals formed by its decomposition in copolymerization reactions with derivatives of methacrylic acid, the initiating radicals attack the methacrylic acid derivative so that a complex radical of the following structure is formed:



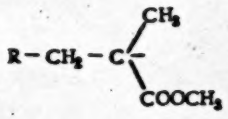
This has its free valency on carbon and can now draw vinyl ethers into a copolymerization reaction. It has been pointed out that the presence of conjugated double bonds in the complex radical referred to above has a favorable influence on the initiation of the copolymerization of vinyl ethers [4, 5].

Apart from these factors, the concentration of the vinyl ether affects the course of the copolymerization process, and as this concentration increases, the proportion of vinyl ether units in the copolymer chain also increases. The extension of our ideas on polymerization and copolymerization has resulted from the direction of our studies to the reactions of compounds similar in general structure, but differing from one another by the presence of different substituents. The enables us to obtain a clear picture of the effects of atoms and groups in the molecules, as expounded in the teaching of Markovnikov [6].

In spite of the fact that methacrylic acid derivatives differ from the corresponding derivatives of acrylic acid only in the presence of the 2-methyl group, there are considerable differences in the courses of the corresponding polymerization and copolymerization reactions and in the properties of the products of these reactions. This gives reason to suppose that the initiating effect of the complex radical



is probably greater than for the corresponding radical from methyl methacrylate



The copolymerization reaction and the properties of the radical have now been studied for methyl acrylate and vinyl ethers as reactants, and it has been found that in this reaction methyl acrylate is more reactive than methyl methacrylate. The polyacrylate differs from the polymethacrylate in that its ester groups can be readily and quantitatively removed by hydrolysis.

Finally, it must be pointed out that the polymers and copolymers obtained are more elastic than the corresponding products obtained from methyl methacrylate. There are only isolated references in the literature to the

copolymerization of methyl acrylate with vinyl ethers [7]. There are references to examples of emulsion copolymerization and to the marketing of a number of commercial products. There are no data relating to the course of these reactions, however: there is only the statement that radicals derived from alkyl vinyl ethers are about the same in activity as that derived from vinyl acetate with respect to their behavior towards methyl acrylate monomer [8]; it is also concluded that alkyl vinyl ethers do not yield macromolecular compounds with, for example, vinyl acetate. Apart from these, there are no data in the literature on the copolymerization of vinyl ethers with methyl acrylate. The copolymerization reactions of vinyl ethers with acrylic acid derivatives are nevertheless of great interest. We have therefore investigated the reactivities of vinyl ethers and methyl acrylate in such reactions. A study of the course of the reactions and the compositions of the copolymers has shown that with increase in the concentration of vinyl ethers in the reaction medium the yields of copolymer fall and the proportion of vinyl ether units in the copolymer chain rises. A comparison of the compositions, structures, and properties of the copolymers of vinyl ethers with methyl methacrylate and with methyl acrylate reveals considerable differences, including the difference in the proportion of ester units in the chain, the proportion of methacrylate residues being the greater (Table 1).

Table 1 gives the compositions of the copolymers, as derived from elementary analysis and the results of the hydrolysis of the ester groups of the methyl acrylate units.

With regard to the properties of the copolymers, it may be noted that copolymers formed by methyl acrylate with alkyl vinyl ethers are more highly elastic than polymethyl acrylate. If, however, the copolymer contains phenyl vinyl ether units, the elasticity is considerably reduced. With respect to elasticity, methyl acrylate polymers and copolymers can be placed in the following series (the formulas are conventionalized):

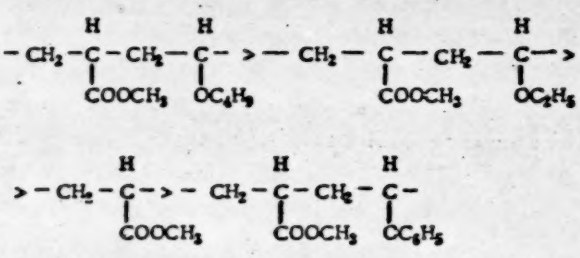
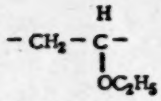
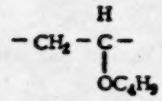
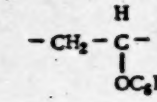
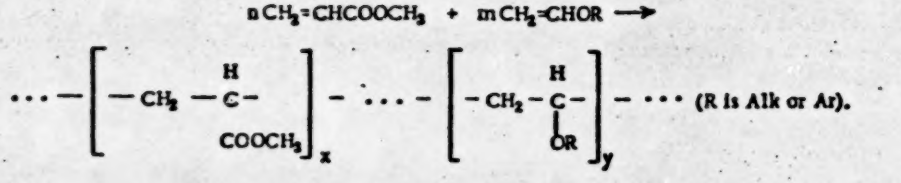


TABLE 1

Comparison of the Compositions of Copolymers of Vinyl Ethers with Methyl Methacrylate and with Methyl Acrylate

Name of residue	Molar percentage of methacrylate or acrylate residues in the copolymer containing the following residues		
			
	(Molar ratio of monomers 1:1)		
Methyl methacrylate	85.35	86.4	81.05
Methyl acrylate	71.8	67.3	72.4
	(Molar ratio of monomers 1:3)		
Methyl methacrylate	78.35	76.33	65.38
Methyl acrylate	55.9	59.1	57.9

The course of the copolymerization of methyl acrylate with a vinyl ether can be represented as follows:



EXPERIMENTAL

The starting materials were freshly distilled and had the following constants:

Methyl acrylate: b. p. 80-81°; n_D^{20} 1.3780; d_4^{20} 0.9550.

Ethyl vinyl ether: b. p. 35.9°; n_D^{20} 1.3778; d_4^{20} 0.7533.

Butyl vinyl ether: b. p. 93.5-93.7°; n_D^{20} 1.4028; d_4^{20} 0.7791.

Phenyl vinyl ether: b. p. 155-156°; n_D^{20} 1.5225; d_4^{20} 0.9765.

Acetone: b. p. 56.5°; n_D^{20} 2.3595.

Methanol: b. p. 64-65°; n_D^{20} 1.3300.

Experimental Procedure. The copolymerization was carried out in sealed glass tubes at 60 ± 1°. Benzoyl peroxide was used as initiator, and the reaction components were taken in various molar ratios. Reaction proceeded continuously for forty hours, when solid or highly viscous products were obtained. When reaction was complete, the tubes were cooled to 0°. Control experiments on the polymerization of the individual starting materials were conductedunder the same conditions. The reaction products were brought into solution and reprecipitated, and were then extracted until there was no longer any reaction for double bonds. The products were then treated with selective solvents and dried to constant weight. The polymerization products were analyzed for carbon and hydrogen, and their compositions calculated.

In order to check the ability of the monomers to undergo free-radical polymerization, some control tests were made.

1. Experiments on the tendency of methyl acrylate to undergo polymerization in presence of benzoyl peroxide were carried out by the above-described procedure. In the first experiments reaction was very violent (with explosion), and the amount of benzoyl peroxide was therefore reduced to 0.05%. The duration of the polymerization was 40 hours. The methyl acrylate polymer was soluble in acetone, less soluble in benzene, and insoluble in methanol, ether, and water. Elementary analysis showed that the purified polymer contained the following amounts of carbon and oxygen:

Found %:	C 55.76; 55.75;	H 7.22; 7.24
Calculated %:	C 55.80;	H 7.00

2. Ethyl, butyl, and phenyl vinyl ethers were heated in presence of benzoyl peroxide for 40 hours. Fractionation yielded the original ethers, and an insignificant resinous residue remained at the bottom of the distilling flask.

I Copolymerization of Methyl Acrylate and Ethyl Vinyl Ether

The reactants were 7.13 g (0.083 mole) of methyl acrylate and 17.87 g (0.248 mole) of ethyl vinyl ether (molar ratio 1:3). The contents of the tube became highly viscous.

The copolymer was tested for solubility in various solvents, and it was found that it dissolved in methanol, but not in gasoline (b. p. 70-80°). It may be noted that polymethyl acrylate is insoluble in methanol. The dried copolymer was analyzed, accurate within 0.0001 g, for carbon and hydrogen contents. Also, by hydrolysis with alcoholic alkali, the content of methyl acrylate residues was determined. After precipitation of the copolymers, the solution was analyzed for its content of ethyl vinyl ether by iodometric titration, which showed the presence of 10.56 g of unchanged ethyl vinyl ether.

The copolymerization of methyl acrylate and ethyl vinyl ether was carried out also at other molar ratios by the procedure described above, with the exception that the amount of benzoyl peroxide was reduced to 0.05%, since the copolymerization was accompanied by an explosion when larger amounts were used. The monomer ratios, yields, and compositions of the copolymers are given in Table 2.

The compositions of the copolymers calculated from the elementary analysis is in accord with the results of the direct determination of methyl acrylate residues, which was carried out by hydrolysis of the copolymer in alcoholic alkali and subsequent back-titration of the alkali with acid.

The proportion of methyl acrylate residues, as calculated from the elementary analysis, is in satisfactory agreement with the value obtained by hydrolysis of the acrylate ester groups with alcoholic alkali.

TABLE 2

Yields and Compositions of Copolymers of Methyl Acrylate and Ethyl Vinyl Ether

Proportions of monomers (mole-%)		Yield of polymer or copolymer (%)	Results of elementary analysis		Proportion of monomer residues in copolymer (mole-%)		Proportion of methyl acrylate residues in copolymer determined by hydrolysis (mole-%)
CH_2=CHCOOCH$_3$	CH_2=CHOC$_2$H$_5$		%C	%H	$-CH_2-\underset{\displaystyle COOCH_3}{\overset{\displaystyle H}{\underset{|}{C}}}-$	$-CH_2-\underset{\displaystyle OC_2H_7}{\overset{\displaystyle H}{\underset{|}{C}}}-$	
100	–	92	55.75	–	100	–	99.9
75	25	87.8	57.08 57.00	7.84 7.77	87.14	12.86	86.48
50	50	72.2	58.34 58.59	8.02 8.01	71.8	28.2	73.96
25	75	45.3	59.79 59.85	8.52 8.48	55.9	44.1	61.3
–	100	Nil	–	–	–	–	–

TABLE 3

Yields and Compositions of Copolymers of Methyl Acrylate and Butyl Vinyl Ether

Proportions of monomers (mole-%)		Yield of polymer or copolymer (%)	Results of elementary analysis		Proportion of monomer residues in copolymer (mole-%)		Proportion of methyl acrylate residues in copolymer determined by hydrolysis (mole-%)
CH_2=CHCOOCH$_3$	CH_2=CHOC$_4$H$_9$		%C	%H	$-CH_2-\underset{\displaystyle COOCH_3}{\overset{\displaystyle H}{\underset{|}{C}}}-$	$-CH_2-\underset{\displaystyle OC_4H_9}{\overset{\displaystyle H}{\underset{|}{C}}}-$	
100	–	92.0	55.76 55.75	7.22 7.24	100	–	99.02
75	25	86.84	58.46 58.54	7.88 7.89	84.9	15.1	81.78
50	50	72.0	61.76 61.51	8.91 8.90	67.3	32.7	61.75
25	75	39.2	62.96 62.68	9.35 9.21	59.1	40.9	53.59
–	100	Nil	–	–	–	–	–

II. Copolymerization of Methyl Acrylate and Butyl Vinyl Ether

The reactants were 5.56 g (0.0646 mole) of methyl acrylate and 19.44 g (0.194 mole) of butyl vinyl ether (molar ratio 1:3). The contents of the tube became very viscous. The copolymerization conditions are described above. The copolymer was tested for solubility in various solvents, and it was shown that the copolymer dissolved in acetone and was precipitated by gasoline (b. p. 70-80°). The copolymer was treated with gasoline until it no longer gave a reaction for double bonds. After being dried to constant weight, the copolymer was analyzed for carbon and hydrogen. The proportion of methyl acrylate residues in the copolymer was determined by hydrolysis

with alcoholic alkali. The results of the analysis and the compositions of the copolymers are given in Table 3.

The solution remaining after the separation of the copolymer was analyzed by the iodometric method for its content of butyl vinyl ether [9]. The copolymerization of methyl acrylate and butyl vinyl ether was carried out also at other molar ratios. The yields and compositions of the copolymers are given in Table 3.

As a check on the method, the methyl acrylate ester groups were hydrolyzed by heating the polymer with alcoholic alkali. The excess of alkali was then back-titrated, and the proportion of ester groups was calculated. When the difference in the methods of determination is considered, the agreement between the results obtained must be regarded as satisfactory

III. Copolymerization of Methyl Acrylate with Phenyl Vinyl Ether

The reactants were 4.9 g of methyl acrylate and 20.1 g of phenyl vinyl ether (molar ratio 1:3). The contents of the tube became very viscous. The copolymerization conditions are described above. The copolymers were dissolved in acetone and precipitated with methanol. They were then treated with methanol until the monomers had been completely removed. The copolymers were then dried to constant weight and analyzed for carbon and hydrogen. The compositions of the copolymers were calculated from these results. Analyses were made also for the contents of methyl acrylate residues, the ester groups being hydrolyzed by heating the polymer with alcoholic alkali.

The compositions of the copolymers calculated from the results of elementary analysis and determined directly were closely in agreement. The copolymerization of methyl acrylate and phenyl vinyl ether was carried out also for other concentrations of the original monomers. The yields and compositions of the copolymers and polymers are given in Table 4.

TABLE 4

Yields and Compositions of Copolymers of Methyl Acrylate and Phenyl Vinyl Ether

Proportions of monomers (mole %)		Yield of polymer or copolymer (%)	Results of elementary analysis		Proportion of monomer residues in copolymer (mole-%)		Proportion of methyl acrylate residues in copolymer determined by hydrolysis (mole-%)
CH_2=CHCOOCH$_3$	CH_2=CHOC$_6$H$_5$		%C	%H	$-CH_2-\underset{\displaystyle COOCH_3}{\overset{\displaystyle H}{C}}-$	$-CH_2-\underset{\displaystyle OC_6H_5}{\overset{\displaystyle H}{C}}-$	
100	–	92.0	57.75	7.20	100	–	–
75	25	77.6	60.65 60.45	6.61 6.57	85.1	14.9	79.8
50	50	58.8	64.03 64.33	6.93 7.09	72.4	27.6	64.04
25	75	33.2	67.98 67.93	6.91 6.68	57.9	42.1	49.30
–	100	Nil	–	–	–	–	–

The solutions remaining after separation of the copolymers were analyzed for the original monomers. Methyl acrylate was determined by hydrolysis with alcoholic alkali, the amount found being 0.28 g.

Phenyl vinyl ether was obtained by fractionation. First of all the organic solvents were driven off in presence of hydroquinone, and then the residue was treated with water, dried with potassium carbonate, and fractionated. A liquid was obtained having b. p. 154-155°, n_D^{20} 1.5220, and d_4^{20} 0.9758 (14.2 g). These constants correspond to phenyl vinyl ether [9]. Films obtained from the copolymer of methyl acrylate and phenyl vinyl ether were friable and had the rubberlike appearance that is characteristic of methyl acrylate polymers.

SUMMARY

1. The conditions required for the copolymerization of methyl acrylate with ethyl, butyl, and phenyl vinyl ethers have been studied. Copolymers of methyl acrylate with ethyl, butyl, and phenyl vinyl ethers have been prepared.

2. It has been shown that the composition of the copolymer obtained depends on the concentrations of vinyl ether and methyl acrylate in the given reation mixture.

3. Copolymers of methyl acrylate with vinyl ethers contain greater molar proportions of the latter than the copolymers of methyl methacrylate with the same vinyl ethers.

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N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

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* See Consultants Bureau Translation, page 931.
** " " " " , page 263.
*** " " " " , page 411.

POLYMERIZATION OF VINYL COMPOUNDS

COMMUNICATION 1. STEPWISE SYNTHESIS OF POLY [BUTYL VINYL ETHER]

M. F. Shostakovsky and V. A. Gladyshevskaya

Our previous investigations have shown that the polymerization reactions of alkyl vinyl ethers proceed by a chain mechanism [1, 2]. We have found recently, however, that under certain conditions alkyl vinyl ethers may polymerize in a stepwise manner [3].

The distinguishing feature of free-radical and ionic chain reactions is the formation of macromolecular compounds whatever the duration of the reaction may be, without formation of products of low molecular weight (dimers, trimers, etc.). Free-radical chain polymerization occurs by the opening of double bonds and the subsequent uniting of the molecules according to the following scheme [4]:

$$RCH=CH_2 + RCH=CH_2 \longrightarrow -\underset{R}{CH}-CH_2-\underset{R}{CH}-CH_2-\text{etc.}$$

Polymerization by the ionic chain mechanism may be represented as follows [2].

$$CH_2=CHX + H^+ \rightarrow CH_3-\overset{+}{C}HX;\quad CH_3-\overset{+}{C}HX + CH_2=CHX \rightarrow CH_3-\underset{X}{CH}-CH_2-\overset{+}{C}HX, \text{ etc.}$$

Chain polymerization of alkyl vinyl ethers provides an excellent synthetic method for the preparation of macromolecular products of any degree of complexity.

The stepwise form of ionic polymerization is of special interest because it permits the preparation of the simplest polymerization products, namely the dimers, trimers, etc. With the aid of these we can study the direction of the addition of the monomers and the structure of the terminal units, and we can determine also the variation in chemical and physical properties as we pass from the monomer to the n-mers.

The characteristic features of stepwise polymerization are, first, the presence of an end group, and second, the transfer of hydrogen atoms or of whole groups as each new molecule of monomer adds [4, 5]. Stepwise polymerization is facilitated by compounds containing mobile hydrogen, such as water, alcohol, etc.

These compounds can play various parts, for they may catalyze the process and may take part in the formation of the terminal units. The presence of traces of water, for example, is sufficient to bring about the polymerization of ethylene oxide, which is very stable in the dry state. The polymerization of ethylene oxide may be presented as follows [6]:

$$CH_2-CH_2 + H_2O \longrightarrow HOCH_2CH_2OH$$

$$HOCH_2CH_2OH + CH_2-CH_2 \rightarrow HOCH_2CH_2OCH_2CH_2OH \quad \text{etc.,}$$

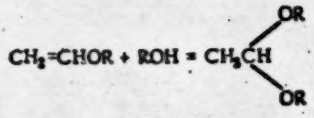
i.e. the process proceeds stepwise.

When studying the behavior of mixtures of butyl vinyl ether and butyl alcohol in a polymerization process, in addition to polymer we isolated 1,1,3-tributoxybutane [3]:

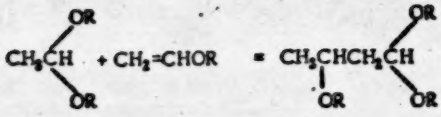
$$CH_3CHCH_2CH(OC_4H_9)_2 \quad (OC_4H_9 \text{ on } CH_3CH)$$

The presence of 1,1,3-tributoxybutane among the reaction products suggested to us that under certain conditions,

i.e. when an alcohol is present, the polymerization of an alkyl vinyl ether is stepwise. The alcohol reacts with the alkyl vinyl ether, and the resulting acetal reacts with more of the ether, yielding 1,1,3,-tributoxybutane:

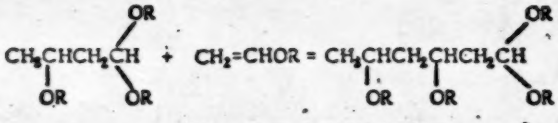


(1)



(2)

The synthesis of acetals from vinyl ethers (Equation 1) is well known and is described in a paper by Shostakovsky and Gershtein [7]. We have carried out the reaction of Equation 2 (the reaction of acetaldehyde dibutyl acetal with butyl vinyl ether) for the specific purpose of explaining the presence of 1,1,3-tributoxybutane in the products of the polymerization of butyl vinyl ether in presence of butyl alcohol [3]. Also, by reaction between 1,1,3-tributoxybutane and butyl vinyl ether it is possible to carry the reaction further with gradual increase in the complexity of the molecule:



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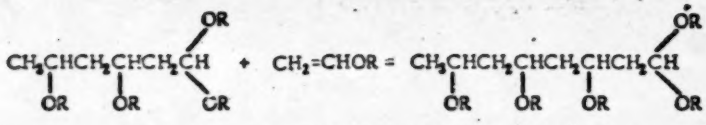


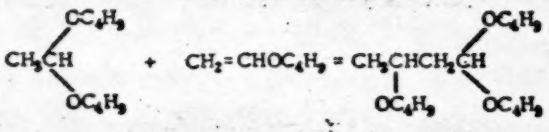
(4)

i.e. the dimer, trimer, and so on are formed successively with already formed end groups. We assume that the end group is an acetal grouping, which is formed, as shown above, by the addition of an alcohol at the double bond.

In order to confirm this view, in the present investigation we have synthesized poly[butyl vinyl ether] having various degrees of polymerization. The first stage consisted in the reaction of acetaldehyde dibutyl acetal with butyl vinyl ether. A similar reaction has been described by Hoaglin and Hirsh [8]. The butoxy compounds so obtained reacted in the successive stages of the reaction with alkyl vinyl ethers.

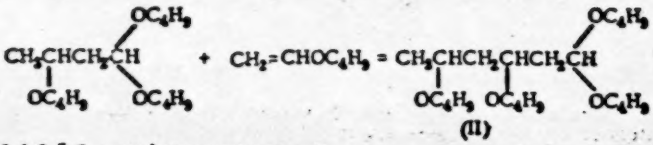
We have carried out the following syntheses:

1) Synthesis of 1,1,3-tributoxybutane:



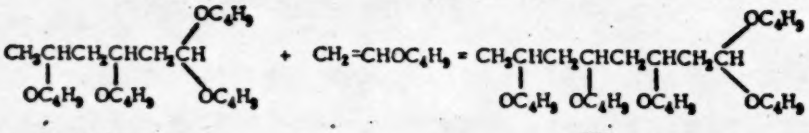
(I)

2) Synthesis of 1,1,3,5-tetrabutoxyhexane:



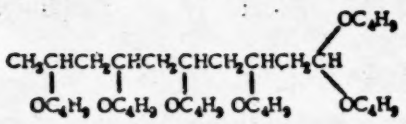
(II)

3) Synthesis of 1,1,3,5,7-pentabutoxyoctane:



(III)

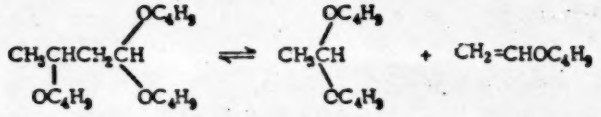
It was shown also that the reaction products (I), (II), and (III) react further with the original butyl vinyl ether and yield still more complex compounds containing the appropriate numbers of butoxyl groups. Thus, in the synthesis of 1,1,3-tributoxybutane some 1,1,3,5-tetrabutoxyhexane was obtained; in the synthesis of 1,1,3,5-tetrabutoxyhexane, some 1,1,3,5,7-pentabutoxyoctane was obtained; and in the synthesis of 1,1,3,5,7-pentabutoxyoctane, a very small fraction (0.6 g) of b.p. 215-220° (3 mm) and n_D^{20} 1.4520 was obtained. It may be assumed that this fraction contained the compound 1,1,3,5,7,9-hexabutoxydecane:



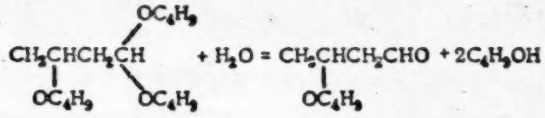
It was not found possible, however, to isolate compounds of higher molecular weight in the pure state, since they decomposed when distilled.

The yields of the compounds formed in these syntheses depend on many of the experimental conditions, particularly the proportion of the reactants. The highest yield of the main product of the synthesis was obtained when the molecular proportions of acetal and vinyl ether were 2:1.

It should be noted that, when the butoxy compounds are repeatedly distilled, they decompose into the original components, so that the processes of polymerization and depolymerization can be represented as follows:



The presence of terminal acetal groups in the synthesized butoxy compounds was established by hydrolysis:



The aldehyde formed was determined quantitatively by the bisulfite method [9]. It was found that the conditions required for the hydrolysis of (I), (II), and (III) were not the same: as the molecular weight rises, milder conditions are needed for the hydrolysis.

EXPERIMENTAL

1. Synthesis of 1,1,3-Tributoxybutane (I). The starting materials were:

a) Acetaldehyde dibutyl acetal, prepared by the condensation of butyl vinyl ether with butyl alcohol in presence of HCl as catalyst [7]. B. p. 185-186° (760 mm); d_4^{20} 0.8263; n_D^{20} 1.4085.

b) Butyl vinyl ether, prepared by the usual method [10]. B. p. 93-94° (760 mm); d_4^{20} 0.7790; n_D^{20} 1.4020.

A 5% solution of ferric chloride in butyl alcohol was used as catalyst.

A mixture of 174 g (1 mole) of the dibutyl acetal and 4 g of a 5% solution of ferric chloride in butyl alcohol was warmed to 48-50° and stirred while 50 g (0.5 mole) of butyl vinyl ether was added dropwise. The rate of addition was controlled so the temperature remained at 48-50°. When the whole of the ether had been added, reaction was allowed to continue for one hour, and the catalyst was then precipitated by anhydrous sodium carbonate powder (4 g). The mixture was stirred for three hours and then filtered. A colorless liquid (215 g) was obtained. On being fractionated under reduced pressure, it yielded

Fraction I	B. p. ..... 67-68° (8mm);	126 g
Fraction II	B. p. ..... 70-135° (5 mm);	2.4 g
Fraction III	B. p. ..... 133-135° (3 mm);	62.3 g
Fraction IV	B. p. ..... 136-173° (3 mm);	1.2 g
Fraction V	B. p. ..... 173-176° (3 mm);	6.6 g
Residue		12.6 g

The intermediate fractions (II and IV) were not investigated because of their small amount.

Refractionation of Fraction I at atmospheric pressure yielded, as the main fraction, acetaldehyde dibutyl acetal, b. p. 184-185° (760 mm): d_4^{20} 0.8259; n_D^{20} 1.4087. The literature [7] gives b. p. 185-186° (760 mm); d_4^{20} 0.8268; n_D^{20} 1.4085.

A second vacuum distillation of Fraction III yielded 1,1,3-tributoxybutane (I), b. p. 134-135° (3 mm): d_4^{20} 0.8655; n_D^{20} 1.4255; MR 81.02; M 266, 262; viscosity 3.573 centipoise. Calculated for $C_{16}H_{34}O_3$ MR 81.017; M 274.

	Found %:	C 70.09; 70.33; H 12.57, 12.44
$C_{16}H_{34}O_3$.	Calculated %:	C 70.00; H 12.49

We have previously prepared 1,1,3-tributoxybutane by a catalytic method [3].

Fraction V was purified by refractionation under reduced pressure, and was found to be 1,1,3,5-tetrabutoxyhexane (II), b. p. 175-177° (3 mm); d_4^{20} 0.8886; n_D^{20} 1.4345; MR 109.88; M 365, 360. Calculated for $C_{22}H_{46}O_4$: MR 109.83; M 374.

2. Synthesis of 1,1,3,5-Tetrabutoxyhexane (II). The reactants were 92 g (0.335 mole) of 1,1,3-tributoxybutane, b.p. 134-135° (3 mm); d_4^{25} 0.8658; n_D^{25} 1.4262, and 11 g (0.11 mole) of butyl vinyl ether. The reaction conditions were the same as those of Experiment No. 1.

The product was 98 g of a slightly colored liquid, which was repeatedly distilled under reduced pressure. As a result, in addition to unchanged 1,1,3-tributoxybutane, the following compounds were obtained:

a) 1,1,3,5-Tetrabutoxyhexane (II) (12.8 g); b. p. 173-175° (3 mm); d_4^{20} 0.8892; n_D^{20} 1.4347; MR 109.57; M 360, 357; viscosity 8.374 centipoise. Calculated for $C_{22}H_{46}O_4$: MR 109.83; M 374

	Found %:	C 70.66; 70.27; H 12.31; 12.40
$C_{22}H_{46}O_4$	Calculated %:	C 70.50; H 12.37

b) 1,1,3,5,7-pentabutoxyoctane (III) (8.3 g); b.p. 195-197° (3 mm); d_4^{20} 0.9033; n_D^{20} 1.4435; MR 139.28; M 467, 463. Calculated for $C_{28}H_{58}O_5$: MR 139.42; M 474.

3. Synthesis of 1,1,3,5,7-Pentabutoxyoctane (III). The reactants were 125 g (0.334 mole) of 1,1,3,5-tetrabutoxyhexane, b.p. 174-175° (3 mm); d_4^{20} 0.8890; n_D^{20} 1.4350, and 16.5 g (0.165 mole) of butyl vinyl ether. The reaction conditions were the same as those of Experiment No. 1. The product was 135 g of a slightly colored viscous liquid, which was distilled repeatedly under reduced pressure. As a result, in addition to unchanged 1,1,3,5-tetrabutoxybutane (91.8 g), 21.8 g of 1,1,3,5,7-pentabutoxyoctane (III) was isolated. It had b.p. 195-197° (3 mm); d_4^{20} 0.9032; n_D^{20} 1.4440; MR 139.60; M 484, 481; viscosity 18.827 centipoise. Calculated for $C_{28}H_{58}O_5$: MR 139.42; M 474.

	Found %:	C 70.35; 70.69; H 12.19; 11.97
$C_{28}H_{58}O_5$	Calculated %:	C 70.83; H 12.31

In an attempt to fractionate the material remaining after the separation of 1,1,3,5,7-pentabutoxyoctane under reduced pressure, we succeeded in obtaining 0.6 g of a substance of b.p. 215-220° (3 mm); n_D^{20} 1.4520. It was not possible to examine this further owing to the small amount and its very high boiling point. It may be assumed that 1,1,3,5,7,9-hexabutoxydecane was present in this fraction.

4. Hydrolysis of the Butoxy Compounds. A small sealed tube containing a weighed amount (0.03-0.04 g) of the substance was introduced into a flask containing 20 ml of 0.2 N sodium bisulfite. The tube was then broken by shaking the flask vigorously. After a certain period of time, the length of which depended on the structure of the butoxy compound, the excess of bisulfite was titrated. For 1,1,3,5,7-pentabutoxyoctane the titration was carried out immediately after the addition of the compound to the bisulfite solution, for 1,1,3,5-tetrabutoxyhexane the titration was carried out after 30 minutes, and for 1,1,3-tributoxybutane it was carried out after one hour.

In each case a control experiment was carried out at the same time. The degree of hydrolysis of the butoxy compound was calculated by the following formula [9]:

$$x = \frac{M(a-b)}{200\,p} \%\text{ of the theoretical value}$$

(a is the volume of 0.1 N iodine used in the control titration (ml); b is the volume of 0.1 N iodine required for the titration of the unchanged bisulfite (ml); p is the weight of substance (g); and M is the molecular weight of the butoxy compound).

The results on the hydrolysis of the butoxy compounds are given in the table.

TABLE 1

Hydrolysis of the Butoxy Compounds

Butoxy compound	Hydrolysis, %
1,1,3-Tributoxybutane	96.0 96.5
1,1,3,5-Tetrabutoxyhexane	97.2 96.8
1,1,3,5,7-Pentabutoxyoctane	97.6 96.9

SUMMARY

1. The stepwise synthesis has been demonstrated of pure substances of various degrees of complexity corresponding to various stages in the synthesis of poly[butyl vinyl ether].

2. The following substances have been isolated and characterized: 1,1,3-tributoxybutane, 1,1,3,5-tetrabutoxyhexane, and 1,1,3,5,7-pentabutoxyoctane.

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N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

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* See Consultants Bureau Translation, p. 299.

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SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

COMMUNICATION 6. VINYL ETHER OF 2-ANILINOETHANOL

M. F. Shostakovsky and I. A. Chekulaeva

A comparative study of the synthesis and reactions of some vinyl ethers of ethanolamines [1, 2, 3] has shown that the vinylation of amino alcohols demands different conditions from those used for unsubstituted aliphatic alcohols. The vinylation products also differ greatly. It was therefore of interest to study the relation between structure and properties for 2-anilinoethanol and its vinyl ether.

Vinylation of 2-anilinoethanol in presence of its potassium derivative as catalyst gave an 83-85% yield of the vinyl ether:

$$C_6H_5NHCH_2CH_2OH + HC{\equiv}CH \longrightarrow CH_2{=}CHOCH_2CH_2NHC_6H_5$$
(I)

When caustic potash was used as catalyst, the yield of vinyl ether was only 47-50%, being reduced on account of much resinification of the reaction products. The presence of solvent had no appreciable effect on the vinylation reaction. It was found that 2-anilinoethanol is not so readily vinylated as unsubstituted aliphatic alcohols [4], but the replacement of a hydrogen atom by a phenyl radical in the amino group of 2-aminoethanol or 2-diethylaminoethanol results in increased reactivity [1, 2]. In order to prove its structure, the vinyl ether of 2-anilinoethanol was subjected to hydrolysis and to hydrogenation, when the following reactions occurred:

$$CH_2{=}CHOCH_2CH_2NHC_6H_5 \xrightarrow{H_2O} CH_3CHO + HOCH_2CH_2NHC_6H_5$$
$$CH_2{=}CHOCH_2CH_2NHC_6H_5 \xrightarrow{H_2} C_2H_5OCH_2CH_2NHC_6H_5$$
(II)

It was found that the vinyl ether of 2-anilinoethanol, unlike the vinyl ethers of other amino alcohols [1, 2, 3], is converted into a cyclic acetal in presence of traces of concentrated hydrochloric acid:

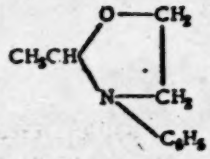
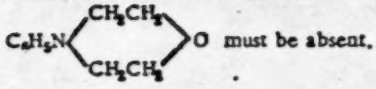
$$CH_2{=}CHOCH_2CH_2NHC_6H_5 \longrightarrow CH_3CH\begin{cases}O-CH_2\\ \\ N-CH_2\\ |\\ C_6H_5\end{cases}$$
(III)

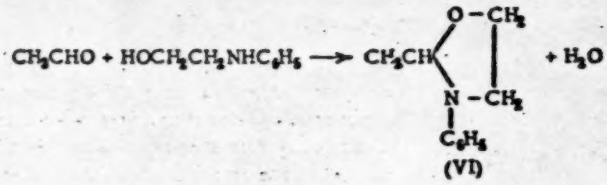
According to the literature [5], cyclization of the vinyl ether of 2-anilinoethanol occurs also when the corresponding amino alcohol is vinylated in presence of cadmium or zinc acetate as catalyst.

When the vinyl ether of 2-anilinoethanol was allowed to react in presence of hydrochloric acid, 2-anilinoethanol (IV) and a substance of composition $C_{12}H_{15}ON$ (V) were isolated in addition to the cyclic acetal. These two substances were formed evidently as a result of the decomposition of the acetal formed by reaction between two molecules of the original vinyl ether:

$$CH_2{=}CHOCH_2CH_2NHC_6H_5 + CH_2{=}CHOCH_2CH_2NHC_6H_5 \longrightarrow$$
$$\longrightarrow \left[CH_3CH\begin{cases}OCH_2CH_2NHC_6H_5\\ \\ NCH_2CH_2OCH{=}CH_2\\ |\\ C_6H_5\end{cases}\right] \longrightarrow HOCH_2CH_2NHC_6H_5 + C_{12}H_{15}ON$$
(IV) (V)

Owing to the readiness with which reactions of this sort occurred, the vinyl ether of 2-anilinoethanol did not unite with alcohols. The synthesis of an acetal from this vinyl ether and an alcohol could not be effected even when heat was applied. The only result was an increase in the yields of 2-anilinoethanol and the compound (V).

The structure of the cyclic acetal (III), which has not been described in the literature, was proved first by hydrolysis with 2% sulfuric acid, which occurred readily and completely at room temperature. The ease of hydrolysis confirmed the oxazolidine structure of the acetal [6]  and showed that the morpholine ring  must be absent. Second, the properties of this acetal were compared with those of 2-methyl-3-phenyloxazolidine (VI), which was prepared by reaction between acetaldehyde and 2-anilinoethanol:

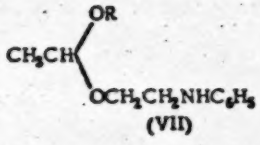


(VI)

This reaction yielded a product of quite definite structure, and it had the same physical and chemical properties as the acetal (III).

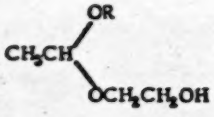
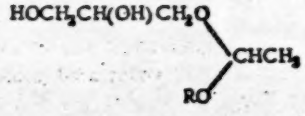
In its tendency to undergo cyclization, the vinyl ether of 2-anilinoethanol is reminiscent of the partial vinyl ethers of glycerol [7] and ethylene glycol [8], but, unlike these reactions, the conversion of the vinyl ether (I) into its cyclic acetal required the catalytic action of concentrated hydrochloric acid and would not take place when the substance was merely heated. Also, this vinyl ether underwent other, more far-reaching changes.

This similarity in properties is found not only in vinyl ethers containing a functional group having a mobile hydrogen atom in the β-position with respect to the oxygen, but also in their derivatives. Thus, the amino acetal of structure

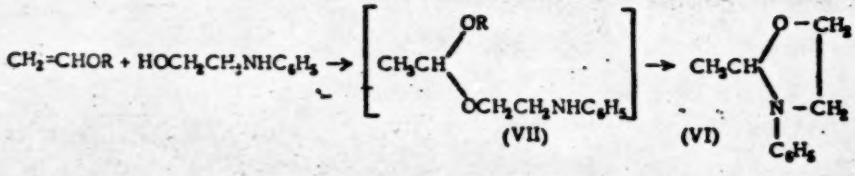


(VII)

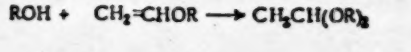
also tends to form cyclic products, like the acetals of ethylene glycol [9] and glycerol [10]:

 and 

Owing to the instability of the amino acetal (VII) under the conditions of the synthesis, we were unable to isolate it by the action of a vinyl ether on 2-anilinoethanol. Only the products of its further reaction were obtained, i.e. the cyclic acetal (VI), the corresponding alcohol (or phenol), and acetaldehyde dialkyl (or diaryl) acetal. These reactions occurred as follows:



(VII) (VI) (1)

 (2)

These reactions were studied in some detail for butyl vinyl and phenyl vinyl ethers.

Among other reactions of the vinyl ether of 2-anilinoethanol, its polymerization was studied. It was found that it would polymerize in presence of 2,2'-azobis(2-methylpropionitrile), but not in presence of ferric chloride and concentrated hydrochloric acid (in the presence of concentrated hydrochloric acid the vinyl ether undergoes other changes, as described above).

EXPERIMENTAL*

1. Synthesis of the Vinyl Ether of 2-Anilinoethanol (I)

2-Anilinoethanol was prepared from aniline and ethylene oxide [11] and had the following constants: b. p. 135° (3 mm); n_D^{20} 1.5798; d_4^{20} 1.0947.

The potassium derivative of 2-anilinoethanol, which was used as a catalyst, was prepared by heating the amino alcohol with potassium at 60-70°. A mixture of 75.5 g of 2-anilinoethanol, 8.3 g of its potassium derivative, and 150 ml of benzene was placed in a steel 2.5-liter autoclave. Acetylene was blown through for a time and then passed in up to a pressure of 14-16 atm. The autoclave was heated to 140-150° and maintained at that temperature for 4-6 hours. The reaction products were vacuum-fractionated, and after removal of benzene the following fractions were collected:

Fraction I	56-117° (7 mm);	n_D^{20} 1.5519;	3.0 g
Fraction II	117-122° (7 mm);	n_D^{20} 1.5530;	85.0 g
Resin			11.4 g

When Fractions I and II were treated with sodium and redistilled, 82.2 g (83.0%) of the vinyl ether of 2-anilinoethanol was obtained. It was a thick colorless liquid, soluble in acetone, benzene, ethanol, and other alcohols, but insoluble in water. It turned yellow when allowed to stand in the air. Its constants were b.p. 116-116.5° (6 mm); 108-109° (3.5 mm); n_D^{20} 1.5523; d_4^{20} 1.0295; MR 50.67; M (cryoscopically in benzene) 151.4; 151.2; Calculated for $C_{10}H_{13}ON$. MR 49.53; M 163.2.

The exaltation of the molecular refraction of the vinyl ether of 2-anilinoethanol and of its derivatives can evidently be explained by the presence of the phenyl radical.

	Found %:	C	73.38;	73.36;	H	8.24;	8.16;	N 8.78, 8.80
$C_{10}H_{13}ON$.	Calculated %:	C	73.59;		H	8.03;		N 8.57

The literature gives: b. p. 128-132° (9 - 10 mm) [5]; b. p. 130-133° (10 mm) [12].

Similar experiments on the vinylation of 2-anilinoethanol were carried out with caustic potash as catalyst, with and without solvent. The results are given in Table 1.

TABLE 1

Dependence of the Yield of the Vinyl Ether of 2-Anilinoethanol on the Vinylation Conditions

Expt. No.	Catalyst (10% on the weight of 2-anilinoethanol)	Solvent	Percent yield of crude vinyl ether (b.p. 117-122°/7 mm)	Resin (% of wt. of aminoalcohol)
1	Potassium derivative	Benzene	83 - 85	13 - 15
2	Caustic potash	Benzene	47 - 50	40 - 45
3	Caustic potash	No solvent	45 - 50	45 - 50

The vinyl ether of 2-anilinoethanol was readily hydrolyzed by 2% sulfuric acid at room temperature. The acetaldehyde so obtained was determined quantitatively by the bisulfite method [13], and the values found for the content of vinyl ether were 98.8 and 98.9%.

Hydrogenation of the vinyl ether (I) over Raney nickel at 120° in an autoclave yielded the ethyl ether of 2-anilinoethanol (II), a thick colorless liquid, b. p. 107-108° (4 mm); n_D^{20} 1.5360; d_4^{20} 1.0002; MR 51.49; calculated for $C_{10}H_{15}ON$ MR 50.02.

	Found %:	C	72.65;	73.01;	H	9.11;	9.07;	N 8.58; 8.71
$C_{10}H_{15}ON$.	Calculated %:	C	72.70;		H	9.15		N 8.47

* M. P. Starshinova, a student of Irkutsk University, assisted in the experimental work.

The literature gives: b. p. 132-136° at 14 mm [12]: b. p. 262-263°; d_{20}^{20} 1.0156 [14].

The polymerization of the vinyl ether in presence of 2,2'-azobis[2-methylpropionitrile] (2% on the weight of the ether) was carried out in a sealed glass tube, which was held continuously at 60-65° for 100 hours. The polymer was separated from unchanged vinyl ether by vacuum distillation. The yield of polymer was 10.4-10.7%; it was a dark-red viscous mass, soluble in ether, benzene, acetone, and alcohols; M (cryoscopically in benzene) 551, 501.

	Found %:	N 8.85; 8.51	
$C_{12}H_{15}ON$.	Calculated %:	N 8.57	

2. Reaction of the Vinyl Ether of 2-Anilinoethanol with Alcohols

The reaction was carried out in a round-bottomed flask fitted with stirrer, thermometer, and reflux condenser. When two drops (0.06 g) of concentrated hydrochloric acid were added to a mixture of 18.5 g (0.113 mole) of the vinyl ether of 2-anilinoethanol and 33.7 g (0.455 mole) of butyl alcohol (b.p. 116-117°; n_D^{20} 1.3990), the temperature rose from 12° to 20°, and it was maintained at this value for three hours. The reaction mixture thickened and became violet in color. The reaction products were vacuum-fractionated:

Fraction I	b.p.	28-31° (3.5 mm);	26.4 g
Fraction II	b.p.	113-135° (6 mm);	9.9 g
Fraction III	b.p.	137-145° (6 mm);	4.4 g
Material collected in trap			6.3 g
Solid residue			4.9 g

Distillation of Fraction I and of the material collected in the trap yielded 32.4 g of butyl alcohol. Refractionation of Fractions II and III under reduced pressure yielded 1.1 g (6% on the amount of vinyl ether taken) of the cyclic acetal (III) and a mixture of 2-anilinoethanol and its vinyl ether.

In order to purify it, the acetal (III) was recrystallized twice from methanol and vacuum-dried (3-5 mm) at 30°, when some of it sublimed, yielding colorless crystals, m.p. 58.5-59.0°; M (cryoscopically in benzene) 160.5; 161.5. Calculated for $C_{10}H_{13}ON$ M 163.2.

	Found %:	C 73.49;	73.49;	H 8.06;	8.01;	N 8.52;	8.60
$C_{12}H_{15}ON$.	Calculated %:	C 73.59;		H 8.02;		N 8.57	

The acetal was found to be soluble in alcohol, ether, benzene, and acetone, and it was readily hydrolyzed by 2% sulfuric acid at room temperature. The acetaldehyde formed in this way was determined quantitatively by the bisulfite method. The results for the content of acetal were 99.44%, 101.0%.

In order to prove the structure of the acetal (III), a mixture melting-point test was done for the acetal and 2-methyl-3-phenyloxazolidine (VI), which was prepared by mixing equimolecular amounts of acetaldehyde and 2-anilinoethanol under cooling. The resulting colorless crystals were purified by recrystallizing them twice from methanol; they melted at 59-59.5°. Hydrolysis with 2% sulfuric acid again went readily and completely, and values of 99.26% and 99.80% were found for the content of 2-methyl-3-phenyloxazolidine. A mixture of the compounds (III) and (VI) melted at 58-59°.

In order to resolve the mixture of 2-anilinoethanol and its vinyl ether, it was treated with gasoline (b.p. 50-100°), which extracted the vinyl ether. Distillation of the residue yielded 1.5 g (9.6% on the amount of the vinyl ether taken) of 2-anilinoethanol (IV), b.p. 132.5° (3 mm) $n_D^{19.5}$ 1.5786.

	Found %:	C 69.81;	70.01;	H 8.18;	8.08;	N 10.24;	10.14
$C_9H_{11}ON$.	Calculated %:	C 70.07;		H 8.03		N 10.20	

The solid residue from the first fractionation of the reaction mixture was dissolved in acetone and reprecipitated with petroleum ether (b.p. 30-50°). Vacuum drying (3-5 mm) yielded 4.6 g (21.4% on the amount of the vinyl ether taken) of a substance that corresponded, according to its analysis, to the compound $C_{12}H_{15}ON$. It was a brown powder of m.p. 96-98°, soluble in acetone, alcohol, and dioxane.

	Found %:	C 76.44;	76.33;	H 8.06;	8.03;	N 7.18;	7.17
$C_{12}H_{15}ON$.	Calculated %:	C 76.16;		H 7.98;		N 7.40	

The reaction of the vinyl ether of 2-anilinoethanol with alcohols was studied also for the alcohol 2-anilinoethanol under various conditions. The behavior of the vinyl ether (I) in presence of concentrated hydrochloric acid

was investigated also in absence of alcohols. The experimental results are given in Table 2.

TABLE 2

Effect of Concentrated Hydrochloric Acid on the Vinyl Ether of 2-Anilinoethanol in Presence and in Absence of Alcohols

Expt. No.	Alcohol	Composition of original mixture (g)		Initial and maximum reaction temperatures (°C)	Duration of reaction (hours)	Yield of reaction products		
		alcohol	vinyl ether			cyclic acetal (III)	the compound $C_{12}H_{15}ON$ (V)	2-anilino ethanol (IV)
						% on amount of ether taken		
1	Without alcohol	–	17.2	20/34	6	5.8	20.0	10.0
2	Without alcohol	–	28.0	100/230	5	13.2	31.2	42.5
3	Butyl alcohol	33.7	18.5	12/20	3	6.0	21.4	9.6
4	Butyl alcohol	30.6	67.5	90/116	27	6.8	25.6	12.8
5	2-Anilinoethanol	26.0	31.0	100/150	4	9.3	21.2	– •

3. Reactions of Alkyl Vinyl Ethers with 2-Anilinoethanol

The reactions of 2-anilinoethanol (b.p. 131.5-132° (3 mm); $n_D^{18.5}$ 1.5800) with alkyl vinyl ethers was carried out in a round-bottomed flask fitted with stirrer, thermometer, and reflux condenser.

a) Reaction of Butyl Vinyl Ether with 2-Anilinoethanol in presence of Concentrated Hydrochloric Acid. Concentrated hydrochloric acid (two drops, i.e. 0.06 g) was added to a mixture of 23.2 g (0.23 mole) of butyl vinyl alcohol (b.p. 93-94°; $n_D^{18.5}$ 1.4025) and 31.7 g (0.23 mole) of 2-anilinoethanol. In the course of one hour the temperature rose from 18° to 28°, and it was maintained at this temperature for 90 minutes. The thick brown reaction mass was vacuum-fractionated, and the following fractions were obtained:

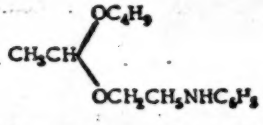
Fraction I B.p. ..... 30 - 50° (4.5 mm); 8.7 g
Fraction II B.p. ..... 108 - 140° (4.5 mm); 11.3 g
Fraction III B.p. ..... 140 - 142° (4.5 mm); 20.8 g
Material collected in trap ..... 6.4 g
Solid resin ..... 7.5 g

Fraction I and the material in the trap were distilled at atmospheric pressure, and yielded:

1) 6.4 g of butyl vinyl ether;

2) 6.5 g (39.2% on the amount of the ether taken) of butyl alcohol, b.p. 116-118°; n_D^{19} 1.4000;

3) 1.1 g of acetaldehyde dibutyl acetal $CH_3CH(OC_4H_9)_2$; b.p. 180-184°; n_D^{19} 1.4088. The acetal was hydrolyzed with 2% sulfuric acid, and the aldehyde liberated was determined by the bisulfite method. The values found for the acetal content were 95.9% and 97.0%. The literature [15] gives b.p. 184-185° (760 mm) and n_D^{20} 1.4090.

Vacuum distillation of Fractions II and III yielded 5.0 g (13.2% on the amount of the ether taken) of 2-methyl-3-phenyloxazolidine (VI), b.p. 57.5-58.5° (see the previous experiment) and 24 g of unchanged 2-anilinoethanol. None of the desired acetal  was isolated.

b) Reaction of Phenyl Vinyl Ether with 2-Anilinoethanol in presence of Concentrated Hydrochloric Acid at 95-100°. Concentrated hydrochloric acid (two drops, i.e. 0.06 g) was added to a hot (94°) mixture of 36.7 g (0.30 mole) of phenyl vinyl ether (b.p. 155-156°; $n_D^{19.5}$ 1.5228) and 42.0 g (0.30 mole) of 2-anilinoethanol. A temperature of 95-100° was maintained for 20 hours. The thick dark-brown reaction mass was vacuum-distilled, and the following fractions were collected:

• 2-Anilino ethanol, in quantity of 31.7 g.

Fraction I	B.p. ..... 40°	(3 mm);	30.3 g
Fraction II	B.p. ..... 40 - 110°	(3 mm);	2.8 g
Fraction III	B.p. ..... 110 - 135°	(3 mm);	38.6 g
Material collected in trap			1.0 g
Solid resin			5.4 g

Fraction I and the contents of the trap were distilled at atmospheric pressure, and yielded 31.0 g of phenyl vinyl ether. Redistillation of Fraction II yielded:

1) 2.0 g (7.0% on the amount of the ether taken) of phenol, b. p. 68-70° at 3 mm, m.p. 41°.

2) 0.4 g (0.8% on the amount of the ether taken) of 2-methyl-3-phenyloxazolidine (VI), m.p. 58-59°.

Fraction III was treated with gasoline (b.p. 50-100°). The gasoline-insoluble part of the fraction (38.2 g) was found to be 2-anilinoethanol. Distillation of the gasoline solution yielded 0.4 g of acetaldehyde diphenyl acetal $CH_3CH(OC_6H_5)_2$, b.p. 135-136° (3 mm) and n_D^{20} 1.5590. The literature [16] gives: b.p. 146-148° (37 mm); n_D^{20} 1.5540; d_4^{20} 1.0808.

SUMMARY

1. The vinylation reaction of 2-anilinoethanol has been studied.

2. The vinyl and ethyl ethers of 2-anilinoethanol have been prepared and characterized.

3. Some of the reactions of the vinyl ether of 2-anilinoethanol have been investigated.

4. It has been found that, unlike other vinyl ethers of ethanolamines, the vinyl ether of 2-anilinoethanol undergoes a series of changes in presence of traces of concentrated hydrochloric acid with formation of 2-methyl-3-phenyloxazolidine, 2-anilinoethanol, and the compound $C_{12}H_{15}ON$.

5. It has been shown that alkyl (or aryl) 2-anilinoethyl acetals, like ethylene glycol and glycerol acetals, are readily converted into cyclic acetals under the conditions of the synthesis.

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N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

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SYNTHESIS OF SULFUR COMPOUNDS

BY THE AID OF VINYL ETHERS AND ACETYLENE

COMMUNICATION 11. ION-CATALYZED REACTIONS OF ETHYL VINYL SULFIDE

M. F. Shostakovsky, E. N. Prilezhaeva, and N. I. Uvarova

Alkyl vinyl sulfides of general formula $RSCH{=}CH_2$, where R is a substituted or unsubstituted alkyl group of any structure and may contain various functional groups, are new compounds that have been little studied. We have previously made a comparative study of some properties of ethyl vinyl sulfide and ethyl vinyl ether, and have shown that, although both of these compounds can undergo free-radical reactions, the tendency to react in this way is more pronounced in ethyl vinyl sulfide [1,2,3]. This view is confirmed by an examination of the polymerization of ethyl vinyl sulfide and its addition reactions with thiols and hydrogen sulfide [3,4]. It is shown in the present paper that reaction of ethyl vinyl sulfide with alcohols, water, and hydrogen halides in presence of ionic catalysts always occurs in accordance with Markovnikovs rule.

The hydrolysis of ethyl vinyl sulfide was carried out in two ways: by means of a weakly acid solution of $NH_2OH \cdot HCl$, i.e., under the conditions used in the quantitative determination of vinyl ethers [5]; and by means of a solution of hydrochloric acid in a mixture of water and dioxane, acetaldehyde being determined in the hydrolyzate by the hydroxylamine method.

It was found that the hydrolysis of ethyl vinyl sulfide by means of a weakly acid solution of hydroxylamine hydrochloride (Equations 1, 2, and 3) requires much more severe conditions (longer time, higher temperature) than those required for ethyl vinyl ether (Table 1). For example, in two hours (the usual time for the quantitative hydrolysis of alkyl vinyl ethers) only 7-10 % of the ethyl vinyl sulfide reacts.

$$CH_2{=}CH{-}SC_2H_5 + H_2O \xrightarrow{H^+} CH_3{-}CHO + C_2H_5SH; \quad (1)$$

$$CH_3{-}CHO + NH_2OH \cdot HCl \longrightarrow CH_3CHNOH + HCl; \quad (2)$$

$$CH_2{=}CHSC_2H_5 + H_2O + NH_2OH \cdot HCl \longrightarrow CH_3CHNOH + C_2H_5SH + HCl. \quad (3)$$

It is easier to attain complete hydrolysis by the second method, but, in presence of HCl, half of the acetaldehyde formed in accordance with Equation 4 then reacts with the thiol that is also formed and yields acetaldehyde diethyl mercaptal (Equation 5). It might be supposed, therefore, that the overall reaction would be as indicated in Equation 6.

$$2CH_2{=}CHSC_2H_5 + 2H_2O \xrightarrow{H^+} 2CH_3CHO + 2C_2H_5SH; \quad (4)$$

$$CH_3CHO + 2C_2H_5SH \xrightarrow{H^+} CH_3CH(SC_2H_5)_2 + H_2O; \quad (5)$$

$$2CH_2{=}CHSC_2H_5 + H_2O \xrightarrow{H^+} CH_3CHO + CH_3CH(SC_2H_5)_2. \quad (6)$$

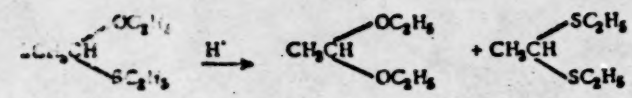
Under the conditions of the reaction, however, the formation of the mercaptal is a reversible process, as will be shown in the experimental part of this paper.

$$CH_3CH(SC_2H_5)_2 + 2H_2O \rightleftharpoons CH_3CHO + 2C_2H_5SH \quad (7)$$

Owing to the superposition of all these reactions, the amount of acetaldehyde in the reaction mixture never corresponds exactly either to Equation 4 or to the overall Equation 6 (see Table 2), so that hydrolysis followed by titration of free acetaldehyde cannot be used for the quantitative determination of ethyl vinyl sulfide.

The reaction of ethyl vinyl sulfide with ethanol was studied. It was found that this reaction is very slow. The resulting monothioacetal is unstable and has a still greater tendency to undergo disproportionation and transetherification reactions (Equation 9 and 10) than the mixed acetals investigated by Shostakovsky and coworkers [1].

$$CH_2{=}CHSC_2H_5 + C_2H_5OH \xrightarrow{H^+} CH_3CH\begin{matrix}OC_2H_5\\SC_2H_5\end{matrix} \quad (8)$$



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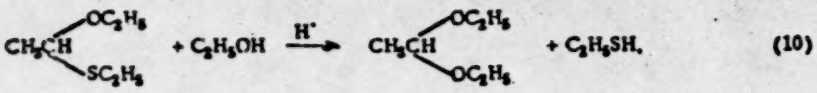

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The addition of ethanol to ethyl vinyl sulfide is therefore accompanied by side reactions, so that only a low yield of the primary product is obtained. This behavior is very different from that of vinyl ethers in their reactions with alcohols, which proceed almost quantitatively.

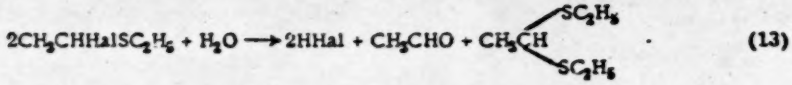
We studied also the reactions of ethyl vinyl sulfide with hydrogen chloride and hydrogen bromide. These reactions were carried out under the conditions already described for the hydrohalogenation of vinyl ethers [1,6]. In both cases high yields of the corresponding ethyl 1-haloethyl sulfides were obtained, i.e., addition of hydrogen halide is in accord with Markovnikov's rule. The hydrohalogenation of ethyl vinyl sulfide differs from that of ethyl vinyl ether in that no marked rise in temperature is to be observed.

$$CH_2{=}CHSC_2H_5 + HCl \longrightarrow CH_3CHClSC_2H_5; \quad (11)$$

$$CH_2{=}CHSC_2H_5 + HBr \longrightarrow CH_3CHBrSC_2H_5. \quad (12)$$

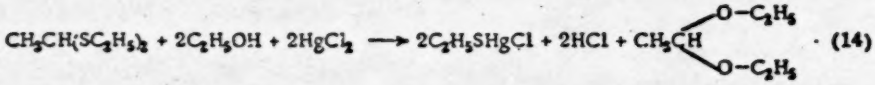
We did not succeed in effecting the addition of hydrogen bromide to ethyl vinyl sulfide in the direction contrary to that required by Markovnikov's rule by carrying out the reaction in an inert solvent in presence of an active free-radical initiator, 2,2'-azobis[2-methylpropionitrile]. Under these conditions a good yield was obtained of the same product as before, 1-bromoethyl ethyl sulfide. Hence, statements in the literature [?] concerning the readiness with which "anomalous" addition reactions occur between hydrogen bromide and vinyl sulfides are inaccurate.

The structures of the synthesized ethyl 1-haloethyl sulfides were proved by a hydrolysis method based on the fact that they are rapidly and quantitatively decomposed by cold water. The great tendency for ethyl 1-haloethyl sulfides to undergo hydrolysis shows how extremely mobile the halogen atoms are in these compounds [8]:



(13)

All of the components of the hydrolyzate can be determined quantitatively: hydrohalic acid, alkalimetrically; acetaldehyde by the hydroxylamine method; and the mercaptal by alkali titration of a solution obtained by addition of excess of ethanolic mercuric chloride (the mercuric chloride method, Equation 14):



(14)

It has been shown already that the halogen of α-halo ethers can be determined quantitatively by titration of their hydrolyzates [6]. The titration of the hydrolyzate forms a method of analysis also for alkyl 1-haloethyl sulfides, since by this means the sulfur and halogen contents of these substances can be determined quantitatively.

1-Chloroethyl ethyl sulfide is more stable to storage than 1-bromoethyl ethyl sulfide, so that the same order is observed here as was observed for α-halo ethers [9]. Dilution with diethyl ether is as effective for the stabilization of these substances as it is for that of their oxygen analogs [9].

It follows from the above discussion that the hydrohalogenation of ethyl vinyl sulfide differs comparatively little from the corresponding reaction of ethyl vinyl ether.

Hence, the ion-catalyzed reactions of ethyl vinyl sulfide with water, alcohol, and hydrogen halides have their specific features, but their general character points to a close analogy between this substance and alkyl vinyl ethers.

EXPERIMENTAL

1. Study of the Conditions Required for the Hydrolysis of Ethyl Vinyl Sulfide

a) Hydrolysis of Ethyl Vinyl Sulfide with 0.5 N $NH_2OH \cdot HCl$ (Equations 1, 2, and 3). The hydrolysis was carried out under conditions similar to those described for alkyl vinyl ethers [5]. A weighed amount (0.15-0.25 g) of ethyl vinyl sulfide was introduced into a flask having a ground-in stopper and containing 10 ml of 0.5 N $NH_2OH \cdot HCl$. The mixture was shaken vigorously for 15 minutes and then maintained at 20-30° for 2-24 hours. Other experiments were carried out at 100° in sealed tubes. The hydrochloric acid liberated was titrated with 0.5 N

TABLE 1

Hydrolysis of Ethyl Vinyl Sulfide with 0.5 N $NH_2OH \cdot HCl$

Expt. No.	Duration of heating, hrs.	Temperature, (°C)	x
1	2	30	4.1
	2	30	3.9
2	24	20 - 30	57.80
	24	20 - 30	67.4
3	0.5	100	72.60
	0.5	100	71.40

TABLE 2

Hydrolysis of Ethyl Vinyl Sulfide in Presence of Hydrochloric Acid

Expt. No.	Duration of heating, hrs.	Temperature (°C)	x
1	1	100	103.6
	1	100	102.1
2	4	100	112.0
	4	100	110.7
3	6	100	108.5
	6	100	108.0
4	11	100	148.2
	13	60	156.4

NaOH with Bromophenol Blue as indicator. As the reaction mixture had a strong odor of ethanethiol, the titration was carried out in a fume cupboard.

The calculation was carried out according to the formula $x = \frac{88.16(a-b)F \cdot 100}{2 \cdot 1000\,p}$ (see Equation 3) (x is the proportion of the ethyl vinyl sulfide that has been hydrolyzed (%); a is the volume (ml) of 0.5 N NaOH having a factor of F required in the titration; b is the acidity of 10 ml of the hydroxylamine solution (ml of the same caustic soda solution); and p is the weight of ethyl vinyl sulfide taken).

b) Hydrolysis of Ethyl Vinyl Sulfide with Hydrochloric Acid (Equations 4, 5, and 6). 1) A mixture of 5.24 g of ethyl vinyl sulfide, 10 ml of 5% HCl, 25 ml of dioxane, and 25 ml of water was heated in a sealed tube in a boiling water bath for six hours. The aqueous layer was separated from the mercaptal and transferred to a measuring flask. The mercaptal was washed out with ether, and the ether solution was washed several times with water and dried over sodium sulfate. Removal of ether and distillation of the residue yielded 3.4 g (76.0% yield according to Equation 6) of acetaldehyde diethyl mercaptal, b.p. 64°-66° (6 mm) and n_D^{25} 1.5023, i.e. having constants close to those given in the literature [10].

Determination of free acetaldehyde in the aqueous solution by the hydroxylamine method gave a value of 0.99 g (75.8%).

2) Using similar conditions but smaller samples of the sulfide (0.3-1 g), we attempted to apply the method for the quantitative determination of ethyl vinyl sulfide. The percentage x of hydrolyzed ethyl vinyl sulfide was determined by titration of the free acetaldehyde in a aliquot of the hydrolyzate by the hydroxylamine method. The calculation was carried out in accordance with Equation 6 by the use of the following formula (in this case, 0.1 N NaOH was used):

$$x = \frac{2 \cdot 88.16\,(a-b)\,F \cdot 100}{10 \cdot 1000 \cdot p}$$ (see Equation 6).

The results are given in Table 2.

It will be clear from Table 2 that after one hour the extent of hydrolysis is fairly close to that required by the overall Equation 6. When heating is more prolonged, the amount of free acetaldehyde increases greatly.

The experiment that we shall now describe shows that this effect is associated with the hydrolysis of the mercaptal that is formed in the first place (Equation 7). Acetaldehyde diethyl mercaptal (0.3368 g) was heated in a closed tube with a mixture of 4 ml of 5% HCl, 25 ml of water, and 25 ml of dioxane under the conditions of Experiment No. 4 (Table 2). The tube was then cooled, and its contents were transferred to a measuring flask. Determination of acetaldehyde by the hydroxylamine method showed that under these conditions hydrolysis of the diethyl mercaptal had occurred to the extent of 34-35%.

2. Investigation of the Conditions required for the Addition of Ethanol to Ethyl Vinyl Sulfide

a) Addition of Ethanol to Ethyl Vinyl Sulfide in presence of SO_2 (Equations 8, 9, and 10). Ethanol (4.6 g, i.e. 0.1 mole) was added to 6 g (0.07 mole) of ethyl vinyl sulfide contained in a three-necked flask fitted with stirrer and reflux condenser. The reaction mixture was cooled to −10°, and a slow current of SO_2 was passed

through it for five minutes. The temperature of the reaction mixture then slowly rose to 24°. The mixture was stirred for 2 hours 30 minutes, and was then set aside overnight. On the next day the mixture was heated for five hours at 60°, and then fractionated. The following fractions were obtained:

Fraction I, in a cooled trap:	4.8 g
Fraction II, b.p. 71-74° (14 mm):	2.8 g
Resinous residue:	2.0 g

Fraction II was acetaldehyde diethyl mercaptal (50% yield). After refractionation it had the following constants: b.p. 67-68° (13mm); n_D^{20} 1.5025; d_4^{20} 0.9706; these are in accord with the data in the literature [10]. Values obtained by the mercuric chloride method (Equation 14) for the content of diethyl mercaptal were 98.1 and 97.6%.

The fraction collected in the trap was fractionated at ordinary pressure and yielded

Fraction I	B.p. 34-74°:	0.3 g; n_D^{20} 1.4025	(odor of ethanethiol)
Fraction II	B.p. 74-78°:	3.5 g; n_D^{20} 1.3815	
Fraction III	B.p. 78-80°:	0.3 g; n_D^{20} 1.3840	
Resinous residue		0.4 g	

Fractions II and III were mixtures of acetaldehyde diethyl acetal and ethanol; this was shown by analysis of these fractions by the hydroxylamine method. The content of the diethyl acetal in these fractions was 45-47%.

Results on the addition of ethanol to ethyl vinyl sulfide in presence of SO_2 at different temperatures are given in Table 3.

TABLE 3

Addition of C_2H_5OH to $CH_2=CH-S-C_2H_5$ in presence of SO_2

Expt. No.	Molar ratio of ethyl vinyl sulfide and alcohol	Duration of heating (hours)	Temperature (°C)	Yield of the diethyl mercaptal (%)
1	1:1.5	6	60	50.0
2	1:1.5	24	20	45.3

b) Addition of C_2H_5OH to Ethyl Vinyl Sulfide in presence of HCl in Dioxane, Aqueous 30% HCl or $CH_3CHBrSC_2H_5$. A mixture of 5 g of ethyl vinyl sulfide and 2.6 g of ethanol was placed in a three-necked flask fitted with a stirrer, and 0.1 g of a solution of HCl in dioxane (25-27%) was added. No rise in temperature was observed. The reaction mixture was stirred for three hours and was then set aside overnight. It was then heated for 90 minutes at 55-60°. It was neutralized with potassium carbonate, and then fractionated, the following fractions being obtained:

Fraction I, in a cooled trap:		3.5 g
Fraction II,	B.p. 25-65° (50 mm):	0.5 g
Fraction III,	B.p. 65-70° (50 mm):	1.3 g
Fraction IV,	B.p. 65-70° (12 mm):	1.1 g

Fractions I and II consisted of mixtures of alcohol, acetaldehyde diethyl acetal, and ethanethiol, for they had the same properties as the fractions obtained in this temperature range in the preceding experiment. Fraction IV was the diethyl mercaptal. Fraction III, boiling range 65-70° (50 mm), was united with several similar fractions from other experiments, and the combined fractions were fractionally distilled. The properties of the substance obtained were b.p. 66.5-67° (46 mm); n_D^{20} 1.4451; d_4^{20} 0.9038; found MR 39.55; calculated MR 39.52.

	Found %:	C	53.57;	53.84;	H	10.47;	10.47;	S 23.72; 23.62
$C_6H_{14}SO$.	Calculated %:	C	53.66;		H	10.51;		S 23.87

These constants coincide with those given in the literature [11, 12] for the monothioacetal. Titration by the mercuric chloride method showed that the fraction contained 98% of the monothioacetal.

The results for the addition of ethanol to ethyl vinyl sulfide in presence of hydrogen chloride in dioxane, of 30% aqueous HCl, and of $CH_3-CHBrSC_2H_5$ are summarized in Table 4 (5-10 g of the sulfide was taken).

c) Reaction of the Monothioacetal with Ethanol in presence of SO_2 (Equation 10). A slow current of SO_2 was passed for five minutes through a cooled (0°) mixture of 6.5 g (0.05 mole) of the monothioacetal and 4.6 g (0.1 mole) of ethanol. No rise in temperature was observed. The mixture was heated at 60-65° for 90 minutes. Two days later it was fractionated, and the following fractions were obtained:

TABLE 4

Addition of C_2H_5OH to $CH_2=CH-S-C_2H_5$ in presence of Hydrogen Chloride in Dioxane, 30% Aqueous HCl, or $CH_3CHBrSC_2H_5$

Expt. No.	Molar ratio of ethyl vinyl sulfide and alcohol	Catalyst (g)	Duration of heating (hours)	Temperature (°C)	Yield of monothioacetal (%)
1	1:1	0.1 g HCl in dioxane (~27%)	1.5	60	20.0
2	1:1.8	" "	48	18	12.0
3	1:1.2	0.1 g HCl (30% aqueous)	48	18	11.0
4	1:1.2	0.1 g $CH_3CHBrSC_2H_5$	48	18	10.5

Fraction I, in cooled trap (42 mm): 4.4 g
Fraction II, B.p. 20-60° (42 mm): 1.9 g
Fraction III, B.p. 50-80° (42 mm): 2.6 g
Fraction IV, B.p. 50-65° (12 mm): 1.0 g
Resinous residue: 1.0 g

Fractions I, II, and III were fractionated at ordinary pressure. They yielded:

Fraction I, B.p. 30 - 44°; 0.2 g
Fraction II, B.p. 44 - 74°; 0.2 g
Fraction III, B.p. 74 - 80°; 5.4 g; n_D^{28} 1.3702
Fraction IV, B.p. 80 - 100°; 1.4 g; n_D^{29} 1.3940
Resinous residue 1.5 g;

Fraction I was ethanethiol. Acetaldehyde diethyl acetal was present in Fraction III to the extent of 32-33%, and in Fraction IV to the extent of 76-77%.

3. Hydrohalogenation of Ethyl Vinyl Sulfide

a) Addition of Hydrogen Chloride (Equation 11). Ethyl vinyl sulfide (9.3 g) was placed in a three-necked flask fitted with stirrer, condenser, and tube for passage of gas, and was cooled to −10°. A current of dry hydrogen chloride. When hydrogen chloride began to leave by the condenser, its passage was discontinued. Fractionation yielded:

Fraction I, B.p. 36-46° (30 mm); 0.6 g
Fraction II, B.p. 46-47° (30 mm); 10.6 g

Fraction II was 1-chloroethyl ethyl sulfide (80.9% yield). After refractionation its properties were b.p. 64-47° (30 mm); n_D^{28} 1.4705; d_4^{28} 1.012; found MR 33.44; calculated MR 33.50.

	Found%*:	Cl 28.41;	28.18;	S 25.13;	25.10
C_4H_9ClS.	Calculated %:	Cl 28.45;		S 25.74	

The following constants are given in the literature for 1-chloroethyl ethyl sulfide: b.p. 42-45° (25 mm) [13] and b.p. 39° (24 mm) [8].

b) Reaction of 1-Chloroethyl Ethyl Sulfide with Water (Equation 13). A weighed amount of 1-chloroethyl ethyl sulfide was introduced into a measuring flask containing water. The contents of the flask were shaken, allowed to stand for 15 minutes, and brought to the mark with alcohol. Hydrogen chloride was determined alkalimetrically, acetaldehyde by the hydroxylamine method, and mercaptal by the mercuric chloride method. The results of the determinations in two parallel experiments are given in Table 5.

TABLE 5

Reaction of 1-Chloroethyl Ethyl Sulfide with Water

Expt. No.	Amount of 1-chloroethyl ethyl sulfide taken (g)	Yield (%)		
		HCl	acetaldehyde	mercaptal
1	1.2340	99.86	98.77	97.67
2	1.2427	99.06	99.36	97.57

* Determined by titration of the hydrolyzate (see Table 6).

1-Chloroethyl ethyl sulfide keeps satisfactorily in a flask having a ground-in stopper for 7-8 days; it then begins to resinify. When diluted with absolute ether, it can be preserved without change for several months.

c) Addition of Hydrogen Bromide (Equation 12) (Experiment No. 1). The addition of HBr was carried out under the same conditions as those used for the addition of HCl. From 8.5 g of ethyl vinyl sulfide, 16.5 g of crude 1-bromoethyl ethyl sulfide was obtained (the theoretical amount was 16.2 g). The excess of hydrogen bromide was removed with the aid of a water pump. Fractionation yielded 12.5 g a substance of b.p. 45-50° (7.5 mm) (residue in flask 2 g). The yield of 1-bromoethyl ethyl sulfide was 77.1%. After refractionation the product had the following constants: b.p. 39-41.5° (5 mm); n_D^{20} 1.5130; d_4^{20} 1.3677; found MR 37.18; calculated MR 36.47

	Found* %:	Br	46.69;	46.64;	S	18.80; 18.70
C_4H_9BrS.	Calculated %:	Br	47.25;		S	18.90

The substance fumed strongly in air, and it began to turn brown after the first day. When diluted with absolute ether it can be preserved without change for several months.

d) Addition of Hydrogen Bromide in a Pentane Medium in presence of 2,2'-Azobis[2-methylpropionitrile] (Experiment No. 2). A mixture of 3.4 g of ethyl vinyl sulfide, 14 g of pentane, and 0.05 g of 2,2'-azobis[2-methylpropionitrile] was prepared in an ampoule. Nitrogen was blown through the ampoule, first at room temperature, and then under cooling. Hydrogen bromide (3.5 g) was then condensed in the ampoule, which was then cooled in liquid nitrogen, evacuated for 20 minutes, and sealed. The ampoule was heated for two hours at 60-70°, and then set aside overnight. Fractionation yielded 5.2 g of a substance of b.p. 45-47° (7 mm); n_D^{20} 1.5130 (residue in flask 0.2 g). The yield was 79.6%.

e) Reaction of 1-Bromoethyl Ethyl Sulfide with Water (Equation 13). A weighed amount of 1-bromoethyl ethyl sulfide was shaken in a measuring flask with 10-15 ml of water for 15 minutes. The determination of the components of the hydrolyzate [HBr, CH_3CHO, and $CH_3CH(SC_2H_5)_2$] was carried out by the methods used for 1-chloroethyl ethyl sulfide. The results of the titrations of the bromo compounds obtained under different conditions are given in Table 6.

TABLE 6

Reaction of 1-Bromoethyl Ethyl Sulfide with Water

Expt. No.	Amount of 1-bromoethyl ethyl sulfide taken (g)	Yield (%)		
		HBr	acetaldehyde	mercaptal
1	1.1436	98.8	99.6	99.6
2	1.6236	98.75	99.3	98.8

Addition of HBr to ethyl vinyl sulfide, both in presence of 2,2'-azobis[2-methylpropionitrile] (Experiment No. 2), and in its absence (Experiment No. 1), proceeds exclusively in the direction required by Markovnikov's rule.

SUMMARY

1. The ion-catalyzed reactions of ethyl vinyl sulfide with water, with ethanol, with hydrogen chloride, and with hydrogen bromide have been studied, and it has been shown that addition occurs in the direction required by Markovnikov's rule, i.e. as in the similar reactions of vinyl ethers.

2. The conditions have been determined for the hydrolysis of ethyl vinyl sulfide. It has been shown that its hydrolysis by a weakly acid solution of $NH_2OH \cdot HCl$ is much slower than that of ethyl vinyl ether. Ethyl vinyl sulfide undergoes hydrolytic decomposition when treated with a solution of HCl in a mixture of water and dioxane, acetaldehyde and acetaldehyde diethyl mercaptal being obtained.

3. A study has been made of the conditions required for the addition of alcohol to ethyl vinyl sulfide with formation of a monothioacetal. Some of the properties of the monothioacetal have been studied.

4. The conditions required for the hydrohalogenation of ethyl vinyl sulfide have been determined. The addition of hydrogen chloride and of hydrogen bromide has been effected with formation of the ethyl 1-haloethyl sulfides in about 80% yield. It has been shown that ethyl 1-haloethyl sulfides are hydrolyzed by water in the cold, with quantitative formation of hydrogen halide, acetaldehyde, and acetaldehyde diethyl mercaptal.

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N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

* Determined by titration of the hydrolyzate (see Table 6).

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 69. DEPENDENCE OF THE PROPERTIES OF POLYAMIDES ON THE EXTENT OF INTERMOLECULAR HYDROGEN BONDING

V. V. Korshak and T. M. Frunze

The great mechanical strength and high melting points of polyamides have been explained by some authors as due to the occurrence of hydrogen bonding between the macromolecules [1, 2, 3]. This view finds support in the fact that the molecular cohesion forces are greatly different for methylene and for amide groups. Thus, for the methylene group the molecular cohesion energy is 1780 cal/mole, and for the amide group it is 16,200 cal/mole[4]. The proportion of amide linkages will therefore play an important part in determining the properties under consideration. Thus, when the properties of polyesters and polyamides derived from adipic acid are compared, the great differences between them are readily seen.

Polyhexamethylene adipate $[-CO-(CH_2)_4-CO-O-(CH_2)_6-O-]_x$ melts at 56° [5], but polyhexamethyleneadipamide $[-CO-(CH_2)_4-CO-NH-(CH_2)_6-NH-]_x$ melts at 250° [6]. Since the melting point provides a measure of the extent of the interaction between macromolecular chains, these values for the melting points indicate the great difference between these compounds. It is clear that the extent of the interaction between the chains will be associated with the proportion of polar amide groups present, and this interaction will be reflected in the value of the melting point. There are data in the literature that illustrate this dependence, and these include the following (Table 1), which relate to polyamides formed by adipic acid with various diamines.

TABLE 1

Polyamide	Formula	Number of methylene groups in the diamine	M.p. (°C)
Polydimethyleneadipamide	$-CO(CH_2)_4CONH(CH_2)_2NH-$	2	308
Polytetramethyleneadipamide	$-CO(CH_2)_4CONH(CH_2)_4NH-$	4	278
Polyhexamethyleneadipamide	$-CO(CH_2)_4CONH(CH_2)_6NH-$	6	250
Polyoctamethyleneadipamide	$-CO(CH_2)_4CONH(CH_2)_8NH-$	8	235
Polydecamethyleneadipamide	$-CO(CH_2)_4CONH(CH_{21})_{10}NH-$	10	230

A second way in which the proportion of hydrogen bonds may be reduced consists in the creation of conditions that inhibit hydrogen-bond formation between amide groups, and this may be effected either by replacement of the amide hydrogen or by variation in the distances between amide linkages. Such variation occurs in mixed polyamides formed by reaction between several diamines and dicarboxylic acids.

The present investigation was undertaken to determine the effect of variation in the extent of hydrogen bonding on the properties of the polyamide.

EXPERIMENTAL PROCEDURE

We prepared mixed polyamides by reaction of 1,6-hexanediamine with a pair of dicarboxylic acids selected from adipic, suberic, azelaic, and sebacic acids. The choice of acids was determined by the need for obtaining polyamides in which the distances between the amide groups would vary within sufficiently wide limits. Among the polyamides so obtained, that obtained by the polycondensation of 1,6-hexanediamine with a mixture of adipic and sebacic acids has been described by Catlin, Czerwin, and Willey [8], and also by Stastny [9]. We may mention here that the melting point curve that we obtained for this system is in agreement with that described in the literature.

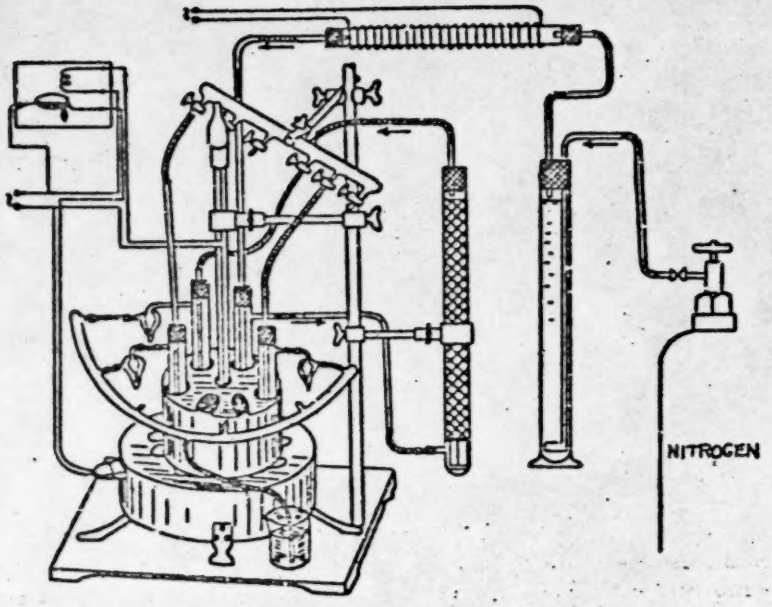

Fig. 1.

Polycondensation was brought about by heating a mixture of the starting materials in a current of pure nitrogen, the temperature being gradually raised from 170-200° to 250-260°, depending on the properties of the starting materials. The heating was carried out in the apparatus shown in Fig. 1. The original substances were placed in test tubes having side arms, which were all connected to one common tube having a single outlet tube, which dipped into water. The nitrogen was carefully purified from oxygen, being passed through an alkaline solution of pyrogallol and a silica tube filled with copper-covered silica gel heated to 450°. The nitrogen was then dried over calcium chloride and phosphoric anhydride and exhaustively purified from oxygen by passage through molten polyamide at 250°. The test tubes were heated in an alloy bath, the temperature being controlled with the aid of an electronic relay.

The melting points of the resulting polyamides were determined by heating small pieces in test tubes under a layer of molten paraffin wax. The test tubes were heated in a glycerol bath, and the rate of rise in temperature was 1-2° per minute. The value obtained for the melting point depends greatly on the rate at which the bath is heated. When heating is rapid, the melting point is considerably depressed, the difference sometimes amounting to 10°. Most mixed polyamides have a very much extended melting range. The substance first softens, then begins to become deformed under external influences, and finally melts. The temperature range from softening to melting varies, but is generally about 10°. The results are shown in Table 2. In addition to the melting points, the solubilities of the polymers in alcohol and in an alcohol-chloroform mixture were determined.

DISCUSSION OF RESULTS

The variation of melting point with composition is shown for the binary systems SubH– AdH, AzH– AdH, SebH– AdH in Fig. 2, and for the system AzH - SebH in Fig. 3*.

As will be seen from Figures 2 and 3, variation in the composition of the polymers results in variation of their melting points and of all of their other properties. Also, a close relationship is to be observed between such properties as melting point and solubility. The melting point falls and passes through a minimum, which corresponds in most cases to a product in which the mole fraction of the substance containing the dicarboxylic acid with the

* The products obtained from the salt SucH differed greatly in their properties from the remaining substances. It is probable that this resulted from differences in the course taken by the reaction. We propose to investigate the causes of this difference.

TABLE 2
Melting Points of the Investigated Binary Systems, °C

Molar ratio of starting substances ••	Starting substances•				
	SucH / AdH	SubH / AdH	AzH / AdH	SebH / AdH	AzH / SebH
1.0/0.0	210 - 212	225 - 227	205 - 208	210 - 212	205 - 208
0.8/0.2	200 - 205	210 - 213	190 - 195	190 - 195	195 - 198
0.6/0.4	200 - 207	197 - 203	178 - 180	185 - 186	180 - 185
0.5/0.5	–	–	185 - 190	190 - 195	178 - 180
0.4/0.6	210 - 215	210 - 215	205 - 208	190 - 197	170 - 175
0.2/0.8	232 - 239	230 - 237	220 - 230	220 - 227	190 - 195
0.0/1.0	250 - 252	250 - 252	250 - 252	250 - 252	210 - 212

• The abreviations used are as follows: Suc - succinic acid; Sub - suberic acid; Az - azelaic acid; Seb - sebacic acid; Ad - adipic acid; H - 1,6-hexanediamine.

•• In these ratios the numerator and denominator correspond to the numerator and denominator respectively of the "fraction" at the top of the column (under "Starting substances").

longer chain is 0.6; i.e. to a content of about 60% by weight of this component.

It should be noted that the position of the minimum is the lower, the greater the length of the dicarboxylic acid molecule from which the original salt is derived. In the system SubH – AdH, for example, the maximum depression in the melting point is 53°, whereas in the system SebH – AdH it is 65°. It follows that sebacic acid, which has ten carbon atoms in its molecule, has a greater effect than suberic acid, which has only eight carbon atoms.

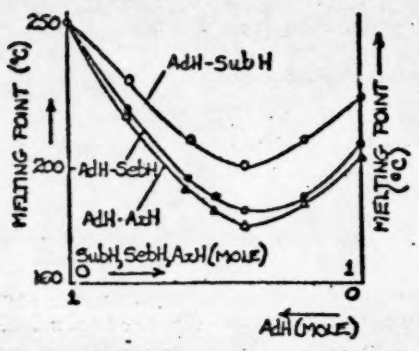

Fig. 2. o) AdH – SubH; •) AdH – SebH; Δ) AdH – AzH

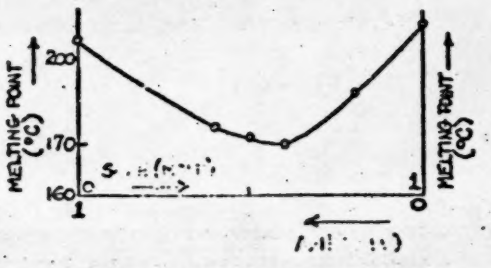

Fig. 3.

In the case of azelaic acid, there is a departure from this rule, for, although it has nine carbon atoms in its molecule (i.e. fewer than sebacic acid), it produces a greater melting point depression in the binary system AdH – AzH than sebacic acid does in the system AdH – SebH. In this first system the minimum melting point is 178°, and in the second 185°. This result evidently arises from the fact that azelaic acid is an "odd" acid, which cannot so readily form hydrogen bonds in the reaction product; we shall consider this matter in greater detail below. In the system SebH – AzH, although we here find the product with the lowest absolute value of melting point (170°), the relative fall in melting point compared with the melting points of the single original salts is only about 40°, i.e. less than in the other systems that we have studied.

All of the products were found to have very low sulubility in organic solvents, with the exception of cresol, in which they are readily soluble. They are readily soluble also in acids (sulfuric, hydrochloric, formic), in dimethylformamide, and in aqueous phenol, i.e. in the solvents in which the polyamides obtained from single 1,6-hexanediamine salts are readily soluble. Solvents may be placed in the following series of reducing solvent power for the system SebH – AzH: cresol, isopropyl alcohol, a mixture of ethanol and chloroform, methanol, ethanol, methyl cellosolve, ethyl cellosolve.

Fig. 4 shows the variation of solubility in a mixture of ethanol and chloroform with composition.

It will we seen from Fig. 4 that the solubility is the greater, the lower the melting point. Thus, the products obtained from the systems we have investigated can be placed in the following series of diminishing solubility: SebH – AzH, AzH – AdH, SebH – AdH, SubH – AdH. The solubilities of the products belonging to the last system are so low that they could not be shown on the graph.

Both the melting points and the solubilities of crystalline polymers are expressions of the interactions between the chains, i.e. of the forces binding the separate macromolecules of the polymer together in the particular sample of the macromolecular compound. The higher the melting point and the lower the solubility of the given polymer, the greater the forces binding the separate molecules to one another; conversely, the lower the melting point and the higher the solubility of the substance, the smaller the forces acting between the separate molecules. Since melting and dissolution are processes in which the crystal lattice of the polymer is disrupted, the readiness with which they occur is related to the strength of the polymer.

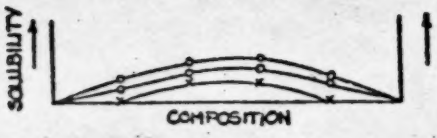

Fig. 4. o) – AzH SebH; •) AdH – AzH; x) AcH SebH

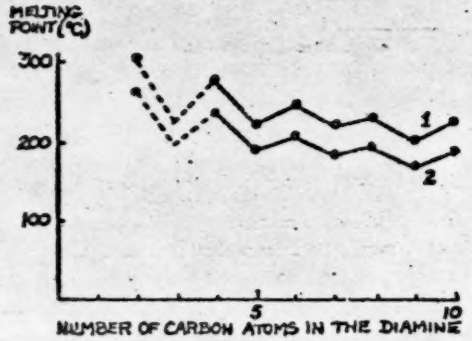

Fig. 5. 1) Polyamides of adipic acid; 2) polyamides of sebacic acid

Polyethylene melts at 110° [10]. Polyamides melt at higher temperatures, and their melting points rise as the length of the repeating unit is diminished, as can be seen from Fig. 5, in which graphs are shown for the dependence of the melting points of the polyamides formed by adipic and sebacic acids with various diamines on the number of carbon atoms in the diamine molecule [11].

It is interesting to note (Fig. 5) that there is a periodic rise and fall in the melting points of the polyamides according as the number of carbon atoms in the diamine is even or odd. The behavior is similar to that of dicarboxylic acids, for polyamides derived from even diamines melt at a higher temperature than the two neighboring polyamides derived from odd diamines. One of us [12] has shown that the melting points of polyesters depend on whether the dicarboxylic acid is even or odd, i.e. a polyester derived from an odd acid melts at a lower temperature than the two neighboring polyesters derived from even acids [13]. Hence, the odd-even effect plays the same part in the diamine series as in the dicarboxylic acid series.

We may conclude, therefore, that the high melting points of polyamides, as compared with polyethylene, are associated with the presence of amide linkages in their molecules. If we actually compare the melting points of the polyamides with the proportions of amide linkages expressed as a percentage of the number of methylene groups in the polyamide chain, we obtained the results given in Table 3.

The absence of data on the melting points of polyamides derived from other dicarboxylic acids prevented us from verifying this relationship more extensively.

The results given in Table 3 relate to polyamides derived from dicarboxylic acids having even numbers of carbon atoms in their molecules, for it was not possible to make use of data relating to polyamides derived from odd dicarboxylic acids owing to the odd-even effect, which would distort the results appreciably. When the data of Table 3 are expressed in the form of a graph in order to show the form of the dependence of melting point on the percentage content of amide linkages in the macromolecular chain, it is found that all of the points fall on a straight line (Fig. 6).

When this straight line is continued, as indicated in Fig. 6 by the broken line, it meets the ordinate axis at 110°, the melting point of polyethylene. There is therefore a linear relationship between the content of amide linkages in the polymer chain and the melting point. Polyethylene, of course, has a zero content of amide linkages,

TABLE 3

Dependence of the Melting Points of Polyhexamethyleneamides on their Percentage Contents of Amide Groupings

Name of polyamide and formula of repeating unit	Number of methylene groups in			Proportion of amide groupings (%)	M.p. of the polyamide (°C)
	the diamine	the acid	the repeating unit of the polyamide		
Polyhexamethyleneadipamide $-NH(CH_2)_6NHCO(CH_2)_4CO-$	6	4	10	20.0	250
Polyhexamethylenesuberamide $-NH(CH_2)_6NHCO(CH_2)_6CO-$	6	6	12	16.6	225
Polyhexamethylenesebacamide $-NH(CH_2)_6NHCO(CH_2)_8CO-$	6	8	14	14.3	210

and we may conclude that the melting point of a polyamide cannot be less than that of polyethylene. The presence of amide linkages results in a rise in melting point that is directly proportional to the proportion of these linkages. It must be remembered, of course, that this conclusion is valid only for polyamides derived from aliphatic dicarboxylic acids and aliphatic diamines having a straight chain not containing any substituents, as the relationship changes considerably for compounds of other types.

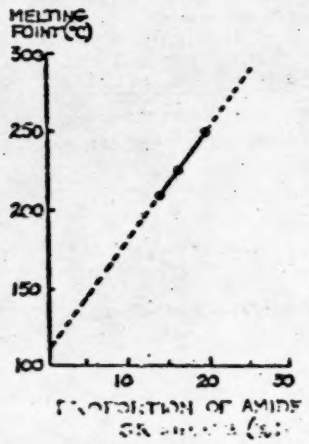

Fig. 6

The presence of amide groupings in the polyamide molecule makes hydrogen bonding possible, and this is responsible for all of the properties attributable to the presence of amide linkages in the molecule. The most important of these are the mechanical properties, the melting point, and the solubility. They are all manifestations of the magnitude of the forces binding the separate molecules together in the mass of the polymer, and the study of them is therefore very important for the complete characterization of the polymer.

For the formation of hydrogen bonds the distribution of amide groupings must be such that the distances between amide groups in neighboring molecules do not exceed 2.7 A, so that it is to be expected that the structure of the polymer chain can greatly affect the ease with which these bonds can arise. Polyamides derived from even and odd amino acids, and also from even and odd diamines and dicarboxylic acids, vary greatly in their melting points. This can be explained simply by the spatial disposition of the amide linkages and the resulting variation in the possibility for the formation of hydrogen bonds [14]. Polyamides derived from odd dicarboxylic acids therefore have lower melting points than those derived from even dicarboxylic acids. For the polyamides formed from mixtures of several dicarboxylic acids, the possibilities for hydrogen-bond formation may vary over a wide range on account of purely spatial factors.

As the proportions of the various units of the polyamide chain are varied, owing to variation in the proportions of the starting materials, the polymer will be found to contain varying proportions of units that differ in their lengths. The distribution of these units in the macromolecular chain must be fairly uniform, according to the results of previous investigations. Thus, one of us, in conjunction with Rafikov [15], Zamyatina [16], Golubev [17], Chelnokova [18], Vinogradova [19], and others, has shown that in various polycondensation reactions of dicarboxylic acids with diamines, glycols, amino alcohols, and other compounds (which occur at high temperature in presence of catalytically active substances, among which are the starting compounds themselves [20]), vigorous exchange reactions occur between the polymer molecules, starting substances, and low-molecular-weight reaction products under the conditions of the process [21]. As a result of these exchange reactions, units of different structure distribute themselves among the various polymer molecules in accordance with thermodynamic probability, which is determined by the number of units of different structure and the size of the polymer molecules [22].

One of us, in conjunction with Chelnokova and Distler [23], carried out the polycondensation of 2-aminoethanol with sebacic acid and obtained a polyamidoester of the same structure as that obtained by the polycondensation of N,N'-bis(2-hydroxyethyl) sebacamide with sebacic acid. This result shows that, owing to the occurrence of exchange reactions during the polycondensation process, a redistribution of the individual units occurs; these units combine with one another in an unrestrained manner and in the order corresponding to the statistical probability of their distribution under the given conditions.

These results give us reason to suppose that polycondensation products present quite a different picture from that presented by copolymers obtained from vinyl monomers, for which convincing proof has been presented both of the nonuniform distribution of monomer residues among the polymer molecules and of their nonuniform distribution along the length of a given macromolecule [24, 25]. We may therefore assume that the polyamides that we have synthesized have molecules of identical structure containing like proportions of the residues of the starting substances distributed more or less uniformly along the length of the macromolecular chain.

These considerations enable us to make a more simple approach to the examination of the possibilities of hydrogen-bond formation between molecules of mixed polyamides. If there were no hindrances to the formation of hydrogen bonds between amide groupings in mixed polyamides, we should expect a smooth variation in melting point within the range of the melting points of the polyamides obtained from the single components. In actual fact, a considerable fall in melting point is observed, and the minimum lies at a mole fraction of 0.6 of the component containing the acid having the longer molecule. The obvious cause for this is the creation of obstacles to the participation of a fraction of the amide groupings in hydrogen bonding. If we examine the structure of the chain of a mixed polyamide, taking the product obtained from the salts SebH and AdH as an example, we may imagine the following distributions of residues in the macromolecule chain for the product containing these salts in the ratio 1:1 :

$$\begin{array}{l} -\text{Ad}-\text{H}-\text{Seb}-\text{H}-\text{Ad}-\text{H}-\text{Seb}-\text{H}-\text{Ad}-\text{H}-\text{Seb}-\text{H}- \\ -\text{Ad}-\text{H}-\text{Ad}-\text{H}-\text{Ad}-\text{H}-\text{Seb}-\text{H}-\text{Seb}-\text{H}-\text{Seb}-\text{H}- \\ -\text{Ad}-\text{H}-\text{Ad}-\text{H}-\text{Seb}-\text{H}-\text{Ad}-\text{H}-\text{Seb}-\text{H}-\text{Seb}-\text{H}- \end{array}$$

and so on. It will be readily seen that the possibilities for the formation of hydrogen bonds in molecules having this sort of structure are considerably less than in those of polyamides derived from a single component. If we replace the symbols in the above representations of the structure by the numbers of carbon atoms in the main chains of the residues denoted by the symbols, we obtain the following picture (the dotted lines indicate hydrogen bonds):

$$\begin{array}{l} -6-8-10-8-6-8-10-8-6-8-10-8- \\ -6-8-6-8-6-8-10-8-10-8-10-8- \\ -6-8-6-8-10-8-6-8-10-8-10-8- \end{array}$$

We may thus show that, owing to the variation in length of the individual components, the opportunities for hydrogen bonding are greatly reduced, and the reduction in the number of such bonds leads to an appreciable fall in melting point. When the ratio of the original salts is 2:3, the opportunities for the formation of hydrogen bonds become even rarer, as can be shown from the same sort of diagrammatic representation:

$$\begin{array}{l} -\text{Seb}-\text{H}-\text{Ad}-\text{H}-\text{Seb}-\text{H}-\text{Ad}-\text{H}-\text{Seb}-\text{H}- \\ -\text{Seb}-\text{H}-\text{Seb}-\text{H}-\text{Seb}-\text{H}-\text{Ad}-\text{H}-\text{Ad}-\text{H}- \\ -\text{Seb}-\text{H}-\text{Seb}-\text{H}-\text{Ad}-\text{H}-\text{Seb}-\text{H}-\text{Ad}-\text{H}- \end{array}$$

or, by the use of figures indicating the numbers of atoms in the units:

$$\begin{array}{l} -10-8-6-8-10-8-6-8-10-8- \\ -10-8-10-8-10-8-6-8-6-8- \\ -10-8-10-8-6-8-10-8-6-8- \end{array}$$

It will be readily seen that in this case the number of hydrogen bonds will be still less than in the previous case, both as a result of the greater number of methylene groups in sebacic acid, which predominates, and also as a result of hindrances of a purely spatial kind to their formation.

These diagrams are only illustrative and cannot be used for the calculation of the proportion of hydrogen bonds. For this purpose we may make use of the graph given in Fig. 6. The points corresponding to the melting points for 1:1 and 3:2 ratios in the system SebH – AdH are 190° and 185°, and have abscissas corresponding to proportions of hydrogen bonds of 11% and 10%. Calculation shows that these polyamides have 16.6% and 16.1% of amide linkages respectively. It may therefore be concluded that, owing to the peculiar features in the structures of mixed polyamides, only 66.2% of the total possible number of hydrogen bonds are realized in the first polyamide, and only 62.1% in the second. The remaining amide groupings are unable to approach one another sufficiently closely for the formation of hydrogen bonds, and their presence, therefore, has no effect on the properties of the polyamide.

SUMMARY

1. A number of mixed polyamides have been investigated from the point of view of the effect of hydrogen bonds on the properties of polyamides, and it has been shown that owing to steric hindrance a considerable proportion

of the amide groupings cannot interact through hydrogen bonds, this fact being reflected in all of the physical properties of the polymer.

2. The properties of mixed polyamide systems have been studied, the substances investigated being products of the reaction of 1,6-hexanediamine with a mixture of two dicarboxylic acids, selected from adipic, succinnic, suberic, azelaic, and sebacic acids.

3. It has been shown that for polyamides derived from a given dicarboxylic acid and various diamines, the melting point varies with the number of carbon atoms in the diamine in accordance with a zig-zag curve, the melting point being higher when the number is even than when it is odd.

4. It has been found that the melting points of polyamides derived from dicarboxylic acids having even numbers of carbon atoms in their molecules vary linearly with the number of amide groupings (i.e. hydrogen bonds).

5. A graphical method has been proposed for the determination of the extent of intermolecular hydrogen bonding in mixed polyamides.

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N. D. Zelinsky Institute of Organic Chemistry
of the USSR Academy of Sciences

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 70. PECULIAR FEATURES OF CHAIN GROWTH DURING POLYCONDENSATION IN PRESENCE OF A CATALYST*

G. S. Kolesnikov, V. V. Korshak and T. V. Smirnova

One of us, in conjunction with Rafikov and Zamyatina [1], has shown that the process of polycondensation is a very complex equilibrium system of reversible reactions. Simultaneously with the chain-growth reaction, which leads to the formation of linear polycondensation products of various molecular weights [2, 4], there occurs also the reverse process – i.e. the destruction of the macromolecular compounds formed by the starting substances – by reaction products of low molecular weight, and by polycondensation products of various molecular weights (dimers, trimers, etc.). It has been established, for example, that polyamides are degraded by carboxylic acids and amines [3], and polyesters are degraded by carboxylic acids, alcohols, and glycols [4].

The rates of the chain-growth and degradation reactions change during the polycondensation process. At the beginning of the process the rate of chain growth greatly exceeds the rate of degradation, but as the polycondensation proceeds the rate of chain growth falls and the rate of degradation rises, so that these rates finally become equal, and a condition of equilibrium is attained. The growth of the polymer molecules then ceases and the molecular weight of the polycondensation products does not rise. The position of equilibrium therefore determines the molecular weight of the final polycondensation products.

Processes of polycondensation and degradation have been studied fairly thoroughly from the point of view of the effect of the nature of the reactants and their proportions [2-5], but the part played by the catalyst in polycondensation processes has not yet been fully elucidated. These processes often occur at high temperatures and in presence of catalysts; or the components themselves may act as catalysts, as acids and glycols do in polyesterification [6]. As would be expected, the choice of catalyst and its concentration are not matters of indifference in polycondensation processes, since the action of the catalyst on different components of the reaction system will be different, and so may affect the position of equilibrium, displacing it in one direction or the other and so determining the molecular weight of the polycondensation products. We have, therefore, investigated the effect of the catalyst on the chain growth of the product of the polycondensation of 1,2-dichloroethane with benzene in presence of aluminum chloride.

We have previously studied [5] the effect of the proportions of the reactants on the properties of the products of the polycondensation of 1,2-dichloroethane with benzene in presence of aluminum chloride. It was found that the molecular weight of poly(ethylenephenyl), the macromolecular product of this polycondensation, increases as the excess of benzene falls. By analogy with other polycondensation reactions it may be supposed that in the polycondensation of 1,2-dichloroethane with benzene, which is always carried out in presence of a catalyst, the formation of poly(ethylenephenyl) will be accompanied by a reaction leading to its degradation. The molecular weight of the poly(ethylenephenyl) obtained will be determined by the position of equilibrium, which, in its turn, will depend not only on the proportions of the reactants, but probably also on the amount of catalyst, since a variation in this amount will affect its concentration in the reaction system, and will therefore alter the rate of degradation and the overall rate of the process. The main reactions occurring in the polycondensation of 1,2-dichloroethane with benzene are as follows:

$$n\mathrm{ClCH_2CH_2Cl} + (n+1)\,\mathrm{C_6H_6} \xrightarrow{\mathrm{AlCl_3}} \mathrm{C_6H_5(CH_2CH_2C_6H_4)_nH} + 2n\mathrm{HCl}.$$

$$\mathrm{C_6H_5(CH_2CH_2C_6H_4)_nH} + m\mathrm{C_6H_6} \xrightarrow{\mathrm{AlCl_3}} (m+1)\,\mathrm{C_6H_5(CH_2CH_2C_6H_4)_{n/m+1}H}$$

The experimental procedure was the same as that used previously [5]. Several series of experiments were carried out, and in each series the proportions of reactants and the reaction conditions remained constant, but the amount of catalyst was varied. The results are given in Tables 1 - 4. In these tables the amount of aluminum chloride used is expressed as a molar percentage of the amount of 1,2-dichloroethane.

It will be seen from Tables 1 - 4 that, in order to obtain a poly(ethylenephenyl) of maximum molecular weight, a definite amount of aluminum chloride must be used for each ratio of the reactants. The use of lower amounts of aluminum chloride either results in low yields of condensation products of low molecular weight, or prevents reaction from occurring.

* This is also Communication 12 of the series, "The Mechanism of the Friedel-Crafts Reaction."

TABLE 1
Polycondensation of 1,2-Dichloroethane with Benzene
(Benzene : dichloroethane = 1.2)

Aluminum chloride (mole-%)	Yield (%) of			Mol. wt. of poly(ethyl-enephenyl)
	Bibenzyl	p-bis(2-phenyl-ethyl) benzene	poly(ethyl-enephenyl)	
0.53	Reaction did not go			
1.06	Reaction did not go			
1.59	6.2	3.5	5.4	1460
2.12	8.4	4.2	8.9	1750
2.65	1.8	1.3	42.2	6740
3.58	2.5	2.7	74.8	6450
5.30	3.7	2.9	56.8	3340

TABLE 2
Polycondensation of 1,2-Dichloroethane with Benzene
(Benzene : dichloroethane = 1.3)

Aluminum chloride (mole-%)	Yield (%) of			Mol. wt. of poly(ethyl-enephenyl)
	Bibenzyl	p-bis(2-phenyl-ethyl) benzene	poly(ethyl-enephenyl)	
0.58	Reaction did not go			
1.15	6.3	4.6	29.5	3040
1.73	3.4	3.0	49.4	4220
2.30	4.0	4.6	66.4	3600
2.88	4.0	4.6	65.6	3650
3.89	4.0	2.5	73.5	4020
5.76	4.1	4.5	74.4	3280

TABLE 3
Polycondensation of 1,2-Dichloroethane with Benzene
(Benzene : dichloroethane = 1.5)

Aluminum chloride (mole-%)	Yield (%) of			Mol. wt. of poly(ethyl-enephenyl)
	Bibenzyl	p-bis(2-phenyl-ethyl) benzene	poly(ethyl-enephenyl)	
0.66	Reaction did not go			
1.33	6.8	5.6	65.8	3310
1.66	6.8	5.6	61.2	3100
1.99	7.3	6.2	71.4	2760
2.65	7.3	6.5	70.5	3080
3.32	6.6	5.9	64.6	2590
4.47	6.8	7.4	68.0	2620
6.63	3.6	0.9	75.5	1880

TABLE 4
Polycondensation of 1,2-Dichloroethane with Benzene
(Benzene : dichloroethane = 2.0)

Aluminum chloride (mole-%)	Yield (%) of			Mol. wt. of poly(ethyl-enephenyl)
	Bibenzyl	p-bis(2-phenyl-ethyl)benzene	poly(ethyl-enephenyl)	
0.88	Reaction did not go			
1.77	3.2	5.8	27.2	3010
2.65	16.8	12.4	60.0	2430
3.53	17.5	8.0	69.2	2740
4.41	14.3	12.1	53.8	2200
5.96	12.8	11.5	52.2	2100

The use of more than the optimum amount of aluminum chloride results in a reduction in the molecular weight of the poly(ethylenephenyl), but does not affect its yield appreciably. The effect of the amount of aluminum chloride taken on the molecular weight of the poly(ethylene-phenyl) is particularly notable when the molar ratio of benzene to dichloroethane is 1.20. When the amount of aluminum chloride is less than 2.6 mole-% of the amount of 1,2-dichloroethane taken, polycondensation either does not occur, or results in the formation of a poly(ethylenephenyl) of low molecular weight in low yield. Increase in the amount of aluminum chloride beyond 4.0-4.5 mole-% on the amount of dichloroethane taken results in a sharp reduction in the molecular weight of the poly(ethylenephenyl).

Our results are probably to be explained as follows. The first stage of the polycondensation of 1,2-dichloroethane with benzene in presence of aluminum chloride is probably the formation of a complex compound of aluminum chloride with 1,2-dichloroethane:

$$ClCH_2CH_2Cl + Al_2Cl_6 \rightleftharpoons ClCH_2CH_2Cl \cdot Al_2Cl_6.$$

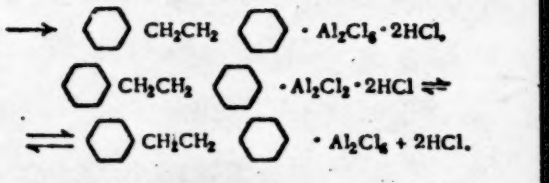
The composition of this complex must actually be less simple, $nClCH_2CH_2Cl \cdot mAl_2Cl_6$ for example, as was shown by one of us and Lebedev [7]. However, for simplicity of exposition, we shall assume the simplest composition $ClCH_2CH_2Cl \cdot Al_2Cl_6$ for the complex, for, in this way, we shall be able to represent the processes occurring during polycondensation more clearly, without distorting in any way the principle upon which our explanation is based. The complex $ClCH_2CH_2Cl \cdot Al_2Cl_6$ reacts further with benzene, forming a ternary complex:

$$ClCH_2CH_2Cl \cdot Al_2Cl_6 + 2C_6H_6 \rightleftharpoons$$
$$\rightleftharpoons ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6.$$

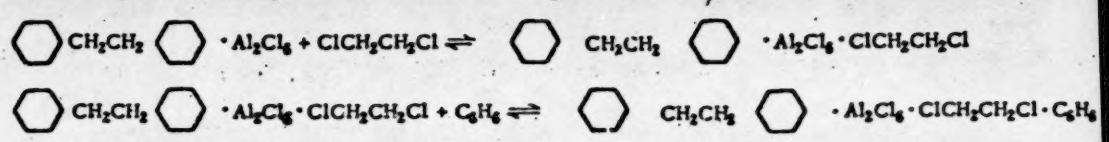
The formation of ternary complexes consisting of an aromatic hydrocarbon, an alkyl halide, and aluminum halide, has been proved by one of us, working with Lebedev and Fedoseev [8].

Reaction between 1,2-dichloroethane and benzene occurs within the ternary complex, and results in the formation of the ternary complex bibenzyl—aluminum chloride—hydrogen chloride:

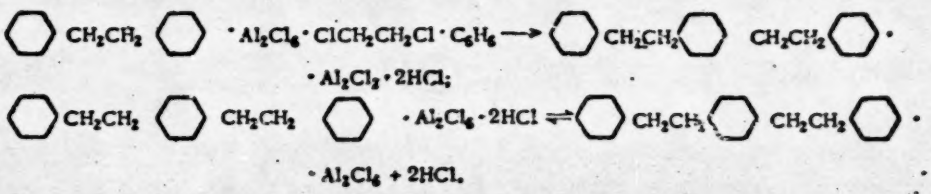
$$ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6 \longrightarrow$$



The complex compound of bibenzyl with aluminum chloride again reacts with dichloroethane and benzene:



Reaction occurs within the complex, and results in the formation of a long chain, hydrogen chloride being evolved:



Further lengthening of the chain occurs in a similar way. In order that the equilibrium

$$ClCH_2CH_2Cl \cdot Al_2Cl_6 + 2C_6H_6 \rightleftharpoons ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6$$

may be displaced to the right to the extent necessary for the amount of ternary complex to be sufficient for rapid reaction within the complex, there must be a sufficiently large excess of one of the original components. When the excess of benzene is small, a definite, fairly large excess of the complex $ClCH_2CH_2Cl \cdot Al_2Cl_6$ must be present in order that the displacement of the equilibrium to the right may be sufficiently large. In its turn, the amount of the complex $ClCH_2CH_2Cl \cdot Al_2Cl_6$ depends entirely on the amount of aluminum chloride, so that for a sufficiently large displacement of the equilibrium to the right, a fairly large amount of aluminum chloride must be used. These considerations are fully in accord with the experimental results. When the excess of benzene is increased, the same shift in the equilibrium to the right may be obtained in presence of a smaller amount of the complex $ClCH_2CH_2Cl \cdot Al_2Cl_6$ than that required in the case considered above. In other words, as the excess of benzene in the mixture of reactants is increased, the amount of aluminum chloride needed for the same shift in the equilibrium will diminish. The experimental results are in good agreement with this conclusion:

TABLE 5

Kinetics of the Degradation of Poly(ethylenephenyl) by Benzene

Duration of degradation (hours)	Yield of poly(ethylenephenyl) (% on weight of original poly(ethylenephenyl)	Mol. wt. of poly(ethylenephenyl)
0	100	3860
1	91	3310
2	78	1820
3	50	1720
5	25	1650
7	23	1280

TABLE 6

Dependence of the Degradation of Poly(ethylenephenyl) on the Amount of Benzene

Proportion by wt. of benzene to poly(ethylenephenyl)	Yield of poly(ethylenephenyl) [% on wt. of original poly(ethylenephenyl)]	Mol. wt. of poly(ethylenephenyl)
0.00	100	3860
0.88	70	2420
2.2	40	2070
4.4	27	2140
8.8	25	1650

It will be seen from Tables 1 - 4 that the smallest amount of aluminum chloride for the formation of a poly(ethylenephenyl) of high molecular weight in satisfactory yield falls in value as the ratio benzene : dichloroethane increases. We consider that the proposed explanation of the course of the reaction is confirmed by the absence of any reaction between 1,2-dichloroethane and benzene in presence of aluminum chloride when the proportions of reactants are dichloroethane : : benzene : aluminum chloride = 2.0 : 0.205 : 0.00615. It is probable that in this case the amounts of aluminum chloride and benzene are insufficient for the formation of the ternary complex $ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6$ in sufficient amount to enable reaction between dichloroethane and benzene to proceed at an appreciable rate.

The amount of aluminum chloride, however, cannot be increased beyond a certain limit without reduction in the molecular weight of the poly(ethylenephenyl) formed. The cause of this reduction in molecular weight may be the degradation of poly(ethylenephenyl) by benzene, which is present in excess, since, under these conditions, two reactions may

occur simultaneously: the polycondensation of 1,2-dichloroethane with benzene, and the degradation of poly(ethylenephenyl) by benzene:

$$nClCH_2CH_2Cl + (n+1)\,C_6H_6 \xrightarrow{AlCl_3} C_6H_5[CH_2CH_2C_6H_4]_nH + 2nHCl;$$

$$C_6H_5[CH_2CH_2C_6H_4]_nH + mC_6H_6 \xrightarrow{AlCl_3} (m+1)C_6H_5[CH_2CH_2C_6H_4]_{n/m+1}H.$$

Some of the laws governing the polycondensation of 1,2-dichloroethane with benzene have been determined by us previously [5]. In order to discover the main laws governing the degradation of poly(ethylenephenyl) by benzene, we have studied the effects of various factors on this reaction, namely, the duration of the reaction, the proportions of the reactants, and the amount of catalyst. It was found that the extent of the degradation for constant proportions of reactants and a constant amount of aluminum chloride depends on the duration of the reaction: the amount of poly(ethylenephenyl) present falls and its molecular weight diminishes, and, simultaneously, the amount of bibenzyl, the reaction product of lowest molecular weight, rises (Table 5, and Fig. 1) (ratio benzene : poly(ethylenephenyl) = 8.8 : 1; the concentration of aluminum chloride was 50% on the weight of poly(ethylenephenyl).

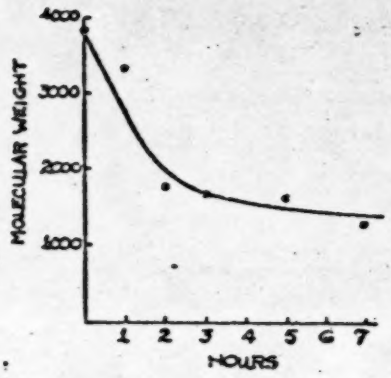


Fig. 1. Kinetics of the degradation of poly(ethylenephenyl) by benzene.

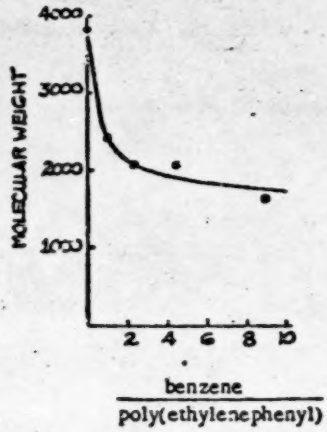


Fig. 2. Effect of the amount of degrading substance (benzene) on the mol. wt. of poly(ethylenephenyl)

A study of the effect of the proportions of reactants, the amount of catalyst and duration of reaction being constant, showed that in this case, as in that of polyamides and polyesters [4], increase in the amount of degrading substance results in a reduction in the amount of poly (ethylenephenyl) and a lowering of its molecular weight. The results of this study are shown in Table 6 and Figures 2 and 3 (the concentration of aluminum chloride was 50% on the weight of poly(ethylenephenyl), and the duration of the reaction was five hours).

It will be seen from Table 6 and Fig. 2 that a great reduction in molecular weight is produced by the action of only small amounts of benzene. A further increase in the amount of benzene has less

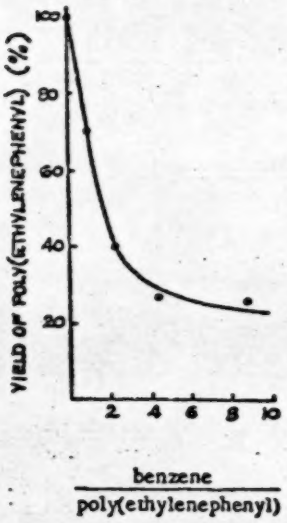


Fig. 3. Effect of the amount of degrading substance (benzene) on the yield of poly(ethylenephenyl).

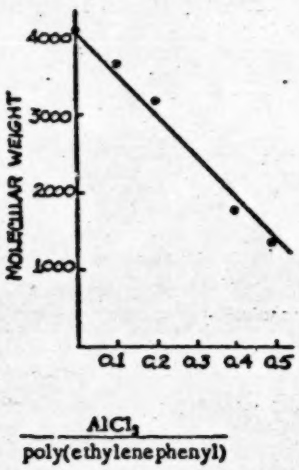


Fig. 4. Effect of the concentration of the degradation catalyst on the mol. wt. of poly(ethylenephenyl)

effect on the molecular weight, which is the usual behavior in degradation reactions [9]. The amount of catalyst used also affects the molecular weight of the poly(ethylenephenyl) and the yield of degradation products. Results of experiments carried out for constant proportions of reactants and for a constant reaction time, but with varying amounts of aluminum chloride, are shown in Table 7 and Fig. 4 (for a reaction time of seven hours).

Table 7 and Fig. 4 show that, as the amount of aluminum chloride is increased, the extent of degradation increases with a resulting fall in the molecular weight of poly(ethylenephenyl). It is clear, therefore, why a reduction was observed in the molecular weight of the poly(ethylenephenyl) obtained when the amount of aluminum chloride was increased beyond its optimum value. This change will result not only in an increase in the concentration of the ternary complex, but also in an increase in the number of degradation centers, so that a poly(ethylenephenyl) of lower molecular weight is obtained. It may, therefore, be regarded as established that the polycondensation of 1,2-dichloroethane with benzene in presence of aluminum chloride is a reversible one, and the position of equilibrium depends on the relative amounts of all components of the reaction system.

TABLE 7

Dependence of the Degradation of Poly(ethylenephenyl) on the Amount of Aluminum Chloride [Benzene: poly(ethylenephenyl) = 8.8 (by weight)]

Ratio of aluminum chloride to poly(ethylenephenyl) (by wt.)	Yield of poly(ethylenephenyl) [% by wt. on original poly(ethylenephenyl)]	Molecular wt. of the poly(ethylenephenyl)
0.0	100	4070
0.1	73	3660
0.2	75	3190
0.4	50	1780
0.5	17.5	1420

SUMMARY

1. It has been shown that the polycondensation of 1,2-dichloroethane with benzene in presence of aluminum chloride is a reversible reaction, the position of equilibrium being determined by the relative amounts of all of the starting substances.

2. It has been shown that poly(ethylenephenyl) is degraded by benzene in presence of aluminum chloride. The laws governing this reaction have been determined.

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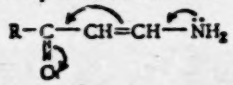
BRIEF COMMUNICATIONS

2-AMINOVINYL KETONES

COMMUNICATION 2. SYNTHESIS OF ALKYL 2-AMINOVINYL KETONES

A. N. Nesmeyanov, N. K. Kochetkov, and Ya. V. Dombrovsky

In previous investigations carried out in our laboratory it has been shown that many possibilities exist for syntheses based on the readily available alkyl 2-chlorovinyl ketones. There can be no doubt that the investigation of alkyl 2-aminovinyl ketones is also of interest in this respect. These compounds are also of theoretical interest, since the conjugation of the carbonyl with the double bond and the free pair of electrons on the nitrogen



would be expected to affect their chemical and physical properties. These compounds may also be found to have practical interest: thus, the use of alkyl 2-aminovinyl ketones as antidetonators has been described [1].

There has been no satisfactory method for the preparation of alkyl 2-aminovinyl ketones. The method based on the action of ammonium salts on 2-hydroxyvinyl ketones [2] cannot be regarded as general, owing to the poor accessibility of these ketones; also, the reaction is often accompanied by the formation of pyridine derivatives, so that the yield of the aminovinyl ketone is greatly reduced [3, 4]. The preparation of alkyl 2-aminovinyl ketones from the corresponding alkyl 2-chlorovinyl ketones by the action of ammonia in anhydrous solvents has been described in the patent literature [5, 6]. After numerous experiments under these conditions, we are convinced that yields of not more than 25% of aminovinyl ketone can be obtained by this method.

We have succeeded in working out a modified method for the synthesis of alkyl 2-aminovinyl ketones from 2-chlorovinyl ketones which makes it possible to prepare them in high yield (78-84%). This was achieved by carrying out the reaction in concentrated aqueous ammonia and continuing to maintain the high concentration of ammonia by continuous saturation of the reaction mixture with gaseous ammonia. This method makes alkyl 2-aminovinyl ketones readily accessible and makes it possible for them to be applied in organic synthesis. Such application will form the object of our further investigations.

Alkyl 2-aminovinyl ketones are high-boiling, colorless oils, which gradually turn yellow. The exaltation of molecular refraction is 3.36-3.55 units for these compounds, which is somewhat lower than the values for alkyl 2-dialkylaminovinyl ketones, which were recently prepared by one of us [7].

All of the alkyl 2-aminovinyl ketones that we have prepared have one very interesting property: the refractive index of the freshly distilled substance rapidly increases until it reaches a limiting value after about 90 minutes. For example, the refractive index of 2-aminovinyl methyl ketone (4-amino-3-buten-2-one) changes from n_D^{20} 1.5462 to n_D^{20} 1.5668. When the sample is redistilled, the refractive index reverts to the lower value and then changes over the same range. It is probable that a tautomeric change occurs, and we are at present investigating the nature of this change.

EXPERIMENTAL

Gaseous ammonia was passed into 600 ml of 25% aqueous ammonia cooled to 0-3° so as to maintain the solution saturated while the alkyl 2-chlorovinyl ketone (0.2 mole) was added dropwise over a period of 20 minutes, the mixture being vigorously stirred and cooled. Stirring was continued for a further two hours, and the mixture was then left in an ice bath for a few hours. The solution was saturated with potassium carbonate and extracted several times with ether (it is best to extract the methyl and ethyl homologs in a liquid extractor). The extract was dried with potassium carbonate, the ether was distilled off, and the residue was vacuum-distilled. The yields, constants, and results of elementary analysis are given in the table for the synthesized alkyl 2-aminovinyl ketones.

Synthesis and Properties of Alkyl 2-Aminovinyl Ketones R–CO–CH=CH–NH_2

R	Yield (%)	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	MR		E_{MR}	Carbon (in %)		Hydrogen (in %)	
					Found	Calc'd		Found	Calc'd	Found	Calc'd
CH_3	84.4••	70 - 71 (3)	1.5668	1.0220	27.19	23.64	3.55	56.53 56.51	56.45	8.51 8.42	8.29
C_2H_5	77.8	72 - 73 (3)	1.5440	0.9893	31.62	28.26	3.36	60.88 60.74	60.59	9.37 9.19	9.15
n-C_3H_7	81.8	84 - 85 (3)	1.5327	0.9650	36.40	32.87	3.53	63.37 63.50	63.64	9.84 9.96	9.79
$(CH_3)_2CH$	80.2	55 - 56 (0.5)	1.5273	0.9610	36.24	32.87	3.37	63.31 63.52	63.64	9.71 9.72	9.79
$(CH_3)_2CH_2CH$	83.5	93 - 99 (2.5)	1.5221	0.9456	41.03	37.49	3.54	66.10 66.21	66.10	10.32 10.33	10.30
n-C_5H_{11}	79.6	103 (2)	1.5160	0.9342	45.65	42.10	3.55	68.05 68.24	68.11	10.88 10.71	10.72

• The values given for the refractive index are the maximum values, measured after the substance has been allowed to stand for two hours.

•• The yield is not reduced when the synthesis is carried out on a larger scale (about two moles of the chlorovinyl ketone).

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M. V. Lomonosov Moscow State University

• See Consultants Bureau Translation, p. 883.

REACTION OF 3-BUTEN-1-YNYLMAGNESIUM BROMIDE WITH HALOTRIPHENYLSILANES

A. D. Petrov, S. I. Sadykhzade, and V. M. Vdovin

A study of the organomagnesium synthesis of 3-buten-1-ynylsilanes [1] has led us to the discovery of considerable difference between the syntheses of trialkyl-(and triphenyl-)3-buten-1-ynylsilanes and those of the corresponding trialkyl-(and triphenyl-)3-buten-1-ynylmethanes. It was found that, whereas the very reactive $(C_6H_5)_3C \cdot Cl$ condenses with $CH_2=CH-C\equiv C \cdot MgBr$ [2], its structural analog $(C_6H_5)_3SiCl$ does not react with the reagent. On the other hand $(CH_3)_3SiCl$ condenses with $BrMgC\equiv C-CH=CH_2$, giving high yields of product, whereas the carbon analog of this chlorosilane $(CH_3)_3C \cdot Cl$ does not react with this Grignard reagent.

With the object of elucidating the causes of this behavior of chlorotriphenylsilanes in synthesis, and also of overcoming the obstacles to the use of compounds containing triphenylsilyl radicals, we have followed two courses: a) introduction into the phenyl radical of a substituent having a positive Hammett constant (for this purpose chlorine was taken; for chlorine $\sigma = + 0.227$ [3]); and b) the replacement of chlorine by fluorine in $(C_6H_5)_3SiCl$.

The idea of replacing chlorine by fluorine was suggested by the fact that the degree of ionization of the Si–F bond is considerably higher than that of the Si–Cl bond [4]. (By taking advantage of this fact, Petrov and Chernysheva [5] were recently able to overcome considerable steric difficulties and effect the syntheses of tetraisopropylsilane, tetracyclohexylsilane, and tetra-1-naphthylsilane.) Both courses led to positive results, and we have synthesized $p\text{-}(ClC_6H_4)_3Si-C\equiv C-CH=CH_2$ and $(C_6H_5)_3Si-C\equiv C-CH=CH_2$, for the first time.

Thus, the difference in reactivity between $(C_6H_5)_3SiCl$ and $(C_6H_5)_3CCl$ is apparently due both to the difference in electron density between the bonds of these siliconium and carbonium radicals with chlorine, and also to the greater steric difficulties in the formation of the siliconium ion.

EXPERIMENTAL

1. 3-Buten-1-ynyltriphenylsilane $(C_6H_5)_2Si-C\equiv C \cdot CH=CH_2$. To $CH_2=CH-C\equiv C \cdot MgBr$, prepared from 12 g of Mg, 54.5 g of C_2H_5Br, and 50 g of $HC\equiv C \cdot CH=CH_2$, 40 g $(C_6H_5)_3SiF$ was added. The last compound was obtained from C_6H_5MgBr and SiF_4; b.p. 207-210°/12 mm; m.p. 60° (for this compound Medoks and Kotelkov [6] give m.p. 64° and b.p. 200-210°/19 mm. When the $(C_6H_5)_3SiF$ was added to the $CH_2=CH-C\equiv CMgBr$ no change could be observed in the reaction mass. The contents of the flask were heated and stirred for two hours, the diluent being diethyl ether. The diethyl ether was replaced by dibutyl ether, and heating was then continued at 80° for eight hours. The product was 38 g (84.5 %) of a substance of m.p. 93°.

Found %: H 5.94; C 85.09; Si 9.27
$C_{22}H_{18}Si$. Calculated %: H 5.81; C 85.01; Si 9.03

2. Chlorotris-(p-chlorophenyl)silane $(ClC_6H_4)_3SiCl$. 1-Bromo-4-chlorobenzene (280 g) was dissolved in ether and added over a period of six hours to a stirred mixture of 40 g of magnesium and 700 ml of ether. Much heat was evolved, and the ether boiled. The resulting Grignard reagent was then added to 70 g of $SiCl_4$. This reaction was also accompanied by the evolution of heat. The reaction mixture was heated for five hours at the boiling point of ether. Ether was then removed, and the mixture was heated for eight hours in a water bath. Fractionation of the residue yielded 25 g (12.5%) of a thick oil, b.p. 242-243°/3 mm, which solidified as a glass, on standing.

Found %: Si 6.88
$C_{18}H_{12}SiCl_4$. Calculated %: Si 7.05

3. 3-Buten-1-ynyltris(p-chlorophenyl)silane $(ClC_6H_4)_3Si-C\equiv C \cdot CH=CH_2$. From 10 g of $(ClC_6H_4)_3SiCl$ and excess of the Grignard reagent $(CH_2=CH-C\equiv C-MgBr)$ 3.5 g (30%) of a crystalline substance of m.p. 107-108° was obtained.

Found %: Si 6.70
$C_{22}H_{15}SiCl_3$. Calculated %: Si 6.75

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N. D. Zelinsky Institute of Organic
Chemistry of the U.S.S.R. Academy of Sciences

SYNTHESIS OF 3- AND 4-ALKENYLTRIALKYLSILANES

V. F. Mironov and N. A. Pogonkina

It can be considered that it is now firmly established that hydrogen halides add to various organosilicon compounds containing the vinyl radical in the direction contrary to that required by Markovnikov's rule [1], whereas they add to allyl derivatives solely in the direction required by the rule [2], even in presence of a peroxide [3].

In the present investigation we have proved the direction of the addition of HBr to a 4-alkenylsilane with the aid of the following reactions:

$$(C_2H_5)_3SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH{=}CH_2 \xrightarrow{HBr} (C_2H_5)_3SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\underset{\displaystyle CH_2}{\underset{|}{C}}HBr \xrightarrow{KOH}$$

$$\longrightarrow (C_2H_5)_3SiCH_2\underset{\displaystyle CH_2}{\underset{|}{C}}HCH{=}CHCH_3 \qquad (1)$$

The difference between the original 4-alkenylsilane and the 3-alkenylsilane formed was established by a comparison of their Raman spectra. Petrov and Nikishin [4] have proposed another method for the preparation of 3-alkenylsilanes. They have synthesized 3-butenyltrimethylsilane (Equation 2), and have shown that HBr adds to this compound in accordance with Markovnikov's rule:

$$(CH_3)_3SiCH_2MgCl + BrCH_2CH{=}CH_2 \longrightarrow (CH_3)_3SiCH_2CH_2CH{=}CH_2 \qquad (2)$$

By this scheme (Equation 2) we have obtained four new 3-alkenylsilanes, including the first 3-alkenylsilane having a double bond at a tertiary carbon:

$$(CH_3)_3SiCH_2MgCl + ClCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 \longrightarrow (CH_3)_3SiCH_2CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2$$

The various trialkyl-1-chloroalkylsilanes (α-chlorides) required as starting materials were synthesized by the action of Grignard reagents on chloro-(1-chloroalkyl)silanes, which have now become accessible [5, 11].

Grignard reagents are obtained from α-chlorides in high yield. From $(C_2H_5)_3SiCHClCH_3$, however, in addition to RMgX, a considerable amount of dimerization product is obtained:

$$2(C_2H_5)_3SiCHCl \xrightarrow{Mg} (C_2H_5)_3SiCH\underset{\displaystyle CH_3}{\underset{|}{}}-\underset{\displaystyle CH_3}{\underset{|}{C}}H(C_2H_5)_3$$

Hence, for the preparation of RMgX from this α-chloride, it is necessary to pour it slowly (100-150 drops/minute) into a 1.5-2-fold excess of magnesium. This tendency for the secondary α-chloride to undergo condensation during the preparation of RMgX is to be associated with analogous properties noted previously by Petrov and Mironov [2] for β- and δ-halides. Molecular refractions calculated from the component values proposed by Warrick [6] show exaltations for our compounds, and these increase as the number of ethyl groups on the silicon atom increase. In order to find a more precise value for the refraction of an Si–C bond in which the C belongs to an ethyl radical, we made use of reliable constants for the alkyltriethylsilane series [7]. It was found that for this series the molecular refraction differs from the calculated value by 0.64% on the average. If, however, the refraction of Si–C in which the C belongs to ethyl is taken to be 2.38 ml/mole instead of the standard value 2.50 [6], the discrepancy is reduced to 0.1%. For convenience in calculation, and also so that it is unnecessary to make an assumption relating the exaltation to a particular bond of the ethyl radical (i.e., to assume which particular bond is polarized), it is desirable to use a value for the refraction of the group Si–C_2H_5, namely 12.08

ml/mole. Results obtained by use of this value in molecular-refraction calculations are given in the table, in which the constants for $(C_2H_5)_3SiCH=CH_2$, which have been redetermined by us, are also given.

In the present investigation we have prepared the first 5-alkenylsilane:

$$(CH_3)_3SiCH_2CH_2CH_2MgBr + BrC_3H_5 \longrightarrow (CH_3)_3SiCH_2CH_2CH_2CH_2CH=CH_2$$

The γ-halide required for this purpose was prepared from $(CH_3)SiCH_2CH_2CH_2OH$ [8], or by the chlorination of trichloropropylsilane. In the only description of the chlorination of $C_3H_7SiCl_3$ given in the literature, SO_2Cl_2 is used [9]. We chlorinated $C_3H_7SiCl_3$ in an apparatus such that the chlorination would actually occur in the liquid phase but the chlorinated product would be removed from the chlorination zone in order to reduce the amount of polychlorides formed [5]. Under these conditions practically no trichloro-1-chloropropylsilane was formed from $C_3H_7SiCl_3$, and the 2- and 3-chloro isomers were formed in ratio 1:0.6. When $C_3H_7SiCl_3$ is chlorinated with sulfuryl chloride [9], the 1-, 2-, and 3-isomers are formed in the proportions of 1:3.5:3.1.

EXPERIMENTAL

Trichloropropylsilane $C_3H_7SiCl_3$ (I). A solution of C_3H_7MgBr prepared from 61 g of Mg (2.51 mole) in 1 liter of ether was added to a cooled solution of 500 g (0.94 mole) of $SiCl_4$ in 500 ml of ether in a 2-liter flask. The flask was set aside overnight. On the next day the contents were filtered from magnesium salts and fractionated, and 275 g (61.5%) of the substance (I), b.p. 123-124°, was obtained. The literature [9] gives b.p. 122-124°, and yield 41%.

Trichloro-2-chloropropylsilane $CH_3CHClCH_2SiCl_3$ (II) and Trichloro-3-chloropropylsilane $ClCH_2CH_2CH_2SiCl_3$ (III.) The substance (I) (274 g) was placed in the flask of the apparatus already described [5]. Chlorination was continued until the temperature in the flask reached 152°, which required seven hours. The rate of passage of chlorine was 200 bubbles per minute. Fractionation through a 30-plate column yielded 90 g of substance (I), b.p. 123°, 114 g of (II), b.p. 162°, and 63.3 g of (III), b.p. 181.5°. The combined yield of (II) and (III) was 81% on the amount of (I) that reacted.

2,2,4,4-Tetramethyl-2,4-disilapentane [10] $(CH_3)_2SiCH_2Si(CH_3)_3$ (IV). 1,1,1,3,3,3-Hexachloro-1,3-disilapropane (142 g) was added dropwise to a cooled solution of CH_3MgI prepared in 1 liter of ether from 94 g of Mg and 600 g of CH_3I. The ether was removed, and the residue was heated in a boiling water bath for four hours. The ether was returned to the flask, and decomposition was effected with water and HCl. The product was 69.5 g (86.3%) of the substance (IV), b.p. 134-134.3°.

(Chloromethyl)trimethylsilane $ClCH_2Si(CH_3)_3$ (V). Dichloro(chloromethyl)methylsilane (163.5 g) was added to a cooled solution of CH_3MgI prepared in 1 liter of ether from 55 g of Mg and 350 g of CH_3I [5]. The contents of the flask were boiled for five hours and then decomposed with water. The products were 93 g (76%) of (V), b.p. 98.5°/765 mm, and 11 g (9%) of (iodomethyl)trimethylsilane [5]. The α-chlorides that follow, and also (chloromethyl)ethyldimethylsilane (VI) and (chloromethyl)diethylmethylsilane (VII), were prepared under similar conditions.

(Chloromethyl)dimethylpropylsilane $ClCH_2Si(C_3H_7)(CH_3)_2$ (VIII). Chloro(chloromethyl)dimethylsilane [5] (38.4 g) was added to C_3H_7MgCl prepared from 6.5 g of Mg in 250 ml of ether. The ether was distilled off, and the mixture was heated at about 100° for eight hours. The product was 22.3 g (55.7%) of (VIII), b.p. 150-151.8°.

	Found %:	C 47.81; 48.00;	H 9.98; 10.09;	Cl 23.21; 23.75;	Si 18.48; 18.33
$C_6H_{13}SiCl$	Calculated %:	C 47.82;	H 10.03;	Cl 23.53;	Si 18.62

(Chloromethyl)methyldipropylsilane $ClCH_2Si(C_3H_7)_2CH_3$ (IX). To C_3H_7MgBr, prepared from 24 g of Mg in 500 ml of ether, 70 g of dichloro(chloromethyl)methylsilane [5] was added. Boiling was for six hours. The product was 54 g (70%) of (IX), b.p. 190-192°.

	Found %:	C 53.73; 53.46;	H 10.50; 10.51;	Cl 19.40; 19.74;	Si 15.34, 15.31
$C_8H_{19}SiCl$	Calculated %:	C 53.75;	H 10.71;	Cl 19.83;	Si 15.69.

3-Chloro-2,2,4,4-tetramethyl-2,4-disilapentane $(CH_3)_2SiCHClSi(CH_3)_3$ (X). To CH_3MgI, prepared from 24.3 g of Mg in 400 ml of ether, 42.5 g of 1,1,1,2,3,3,3-heptachloro-1,3-disilapropane [11] was added dropwise. The ether was distilled off, and the residue was heated at about 100° for three hours. The ether was returned to the flask, and the usual treatment yielded 13 g (50%) of (X), b.p. 177-178.5°. It was not found possible to obtain (X) by the chlorination of (IV) with SO_2Cl_2, although very vigorous chlorination occurred.

	Found %:	Si 28.76; 28.46.
$C_7H_{19}Si_2Cl$	Calculated %:	Si 28.81.

TABLE

No.	Formula of compound	Reference No.	Yield (%)	B.p. in °C (p in mm Hg)		n_D^{20}	d_4^{20}	MR				
								Found	Calc'd [6]	Δ	Calc'd by us	Δ
1	$CH_3CH_2CH_2SiCl_3$	(I)	61.5	123.0	(747)	1.4309	1.1993	38.31	38.43	0.12	–	–
2•	$(CH_3)_2C_2H_5SiCH_2Cl$	(VI)	86	127.8	(757)	1.4295	0.8924	39.52	39.75	0.23	39.63	0.11
3•	$CH_3(C_2H_5)_2SiCH_2Cl$	(VII)	83.7	155.2	(763)	1.4402	0.9029	44.00	44.38	0.38	44.14	0.14
4	$(C_2H_5)_3SiCH_2Cl$	–	71	179.2	(743)	1.4480	0.9101	48.45	49.01	0.56	48.65	0.20
5•	$C_3H_7(CH_3)_2SiCH_2Cl$	(VIII)	55.7	151.7	(753)	1.4335	0.8891	44.18	44.38	0.20	–	–
6•	$(C_3H_7)_2CH_3SiCH_2Cl$	(IX)	70	192.0	(750)	1.4450	0.8902	53.44	53.64	0.20	–	–
7•	$(CH_3)_3SiCHSi(CH_3)_3$	(X)	50	178.5	(747)	1.4489	0.8900	58.70	58.64	0.06	–	–
8•	$(C_2H_5)_3SiCH_2\underset{Cl}{C}HCH{=}CHCH_3$	(XI)	73.9	21[illegible]	(745)	1.4502	0.8016	66.54	66.85	0.31	66.49	0.05
9•	$C_2H_5(CH_3)_2SiCH_2CH_2\underset{CH_3}{C}H{=}CH_2$	(XII)	47.5	140 - 141	(756)	1.4257	0.7550	48.22	48.33	0.11	48.21	0.01
10•	$(C_2H_5)_2CH_3SiCH_2CH_2\underset{CH_3}{C}H{=}CH_2$	(XIII)	68	166.3	(736)	1.4364	0.7743	52.82	52.96	0.14	52.72	0.10
11•	$(C_2H_5)_3SiCH_2CH_2\underset{CH_3}{C}H{=}CH_2$	(XIV)	71	189.5	(755)	1.4437	0.7918	57.22	57.59	0.37	57.23	0.01
12•	$(C_2H_5)_3SiCHCH_2\underset{CH_3}{C}H{=}CH_2$	(XV)	28	207.5	(755)	1.4522	0.8108	61.36	61.85	0.49	61.49	0.13
13•	$(CH_3)_3SiCH_2CH_2\underset{CH_3}{C}{=}CH_2$	(XVI)	51.5	134.6	(750)	1.4235	0.7541	48.10	48.33	0.23	–	–
14•	$(CH_3)_3SiCH_2CH_2CH_2CH_2\underset{CH_3}{C}H{=}CH_2$	(XVIII)	41.5	158 - 159	(750)	1.4246	0.7566	52.78	52.96	0.18	–	–
15•	$(C_2H_5)_3SiCH{-}CHSi(C_2H_5)_3$	(XVII)	15	294 - 297	(750)	1.4752	0.8573	94.15	95.47	1.32	94.75	0.60
16	$(C_2H_5)_3SiC(CH_3){=}CH_2$	–	–	146.5	(745)	1.4345	0.7728	47.99	48.33	0.34	47.97	0.02

• This compound has been prepared for the first time.

Triethyl(2-methyl-3-pentenyl)silane ($C_2H_5)_3SiCH_2\underset{CH_3}{C}HCH{=}CHCH_3$ (XI). A mixture of 45 g of (4-bromo-2-methylpentyl)triethylsilane [2] and 90 g of 30% ethanolic KOH was placed in an autoclave. The autoclave was

rotated and heated at 170-180° for ten hours. The contents were poured into water. Fractionation of the organic layer yielded 22 g of (XI), b.p. 214.5°/745 mm, the yield being 73.9% on the amount of the 4-bromo compound that reacted. The spectra, which were determined by Yu. P. Egorov, indicated the absence of 4-alkenylsilane and showed that cis and trans isomers were present.

3-Butenylethyldimethylsilane $CH_2=CHCH_2CH_2SiC_2H_5(CH_3)_2$ (XII). Allyl bromide (60 g, i.e. an excess so as to deal with any excess of magnesium) was added to a cooled Grignard reagent prepared from 10.7 g of Mg and 56.5 g of (VI) in 250 ml of ether. The contents of the flask were set aside overnight, and on the next day, the ether was distilled off. It was found that distillation of the ether immediately after the addition of C_3H_5Br sometimes results in the ejection of the contents of the flask, but this does not occur when the mixture is left overnight so that the greater part of the C_3H_5Br has reacted. The solid residue was heated in a boiling water bath for five hours. The usual treatment and distillation through a sodium column yielded 45.4 g (77.5%) of (XII), b.p. 140-141°.

	Found %:	C 68.05; 68.05;	H 12.96; 12.88;	Si 19.52; 19.68
$C_6H_{18}Si$.	Calculated %:	C 67.53;	H 12.75;	Si 19.72

The other 3-butenylsilanes were obtained in a similar way.

3-Butenyldiethylmethylsilane $CH_2=CHCH_2CH_2Si(C_2H_5)_2CH_3$ (XIII). To RMgX, prepared in 500 ml of ether from 12 g of Mg and 75 g of (VII), 70 g of C_3H_5Br was added. The contents of the flask were set aside over night and were then boiled, without removal of ether, for three hours. The product was 49 g (68%) of (XIII), b.p. 165-167°.

	Found %:	C 69.83; 69.54;	H 13.23; 13.08;	Si 17.68; 17.47
$C_9H_{24}Si$.	Calculated %:	C 69.15	H 12.89;	Si 17.95

3-Butenyltriethylsilane $CH_2=CHCH_2CH_2Si(C_2H_5)_3$ (XIV). To RMgX, prepared in 250 ml of ether from 6.7 g of Mg and 45 g of (chloromethyl)triethylsilane [5], 50 g of C_3H_5Br was added. On the next day the ether was distilled off and the residue was heated at about 100° for five hours. The product was 33 g (71%) of (XIV), b.p. 188-190°.

	Found %:	C 70.17; 70.29;	H 12.85; 12.95;	Si 15.98; 15.92
$C_{10}H_{22}Si$.	Calculated %:	C 70.51;	H 13.02	Si 16.47

Triethyl(1-methyl-3-butenyl)silane $(C_2H_5)_3SiCHCH_2CH=CH_2$ (XV). (1-Chloroethyl)triethylsilane [5] (523 g) was added slowly to 11 g of Mg in 300 ml of ether. To this Grignard reagent, 35.4 g of C_3H_5Br was added. The ether was driven off, and the residue was heated at about 100° for five hours. The product was 15 g (28%) of (XV), b.p. 206-208°.

	Found %:	C 70.85; 71.04;	H 12.94; 12.95;	Si 14.52; 14.80
$C_{11}H_{24}Si$.	Calculated %:	C 71.66;	H 13.12	Si 15.22

There was a heavy residue of 8 ml. This was insoluble in concentrated H_2SO_4 [see (XVII)].

Trimethyl(3-methyl-3-butenyl)silane $CH_2=C(CH_3)-CH_2CH_2Si(CH_3)_3$ (XVI). 2-Methylallyl chloride (40 g) was added to RMgX prepared from 7 g of Mg and 36 g of (V) in 250 ml of ether. The ether was removed, and the residue was heated at about 100° for about six hours. The product was 21.5 g (51.5%) of (XVI), b.p. 134-134.6°.

	Found %:	Si 19.47; 19.42
$C_8H_{18}Si$.	Calculated %:	Si 19.72.

3,3,6,6-Tetraethyl-4,5-dimethyl-3,6-disilaoctane $(C_2H_5)_3SiCH(CH_3)-CH(CH_3)Si(C_2H_5)_3$ (XVII). (1-Chloroethyl)-triethylsilane (59 g) was added to 8 g of Mg over a period of 40 minutes. Reaction with Mg was initiated by addition of 1 ml of C_2H_5Br. A white precipitate formed during the preparation of RMgX. The ether was removed, and the residue was heated at about 100° for two hours. The complex was decomposed with water, the ether was removed, and the residue was treated with H_2SO_4. The sulfuric acid layer was poured into water, and 15 g of hexaethyldisiloxane separated. The portion

insoluble in sulfuric acid (29 g) consisted of 19.2 g (40%) of tetraethylsilane and 7.1 g (15%) of (XVII), b.p. 293-298°.

	Found %:	C 67.44; 67.61;	H 13.24; 13.37;	Si 19.23; 19.59
$C_{15}H_{32}Si_2$.	Calculated %:	C 67.05;	H 13.36	Si 19.58

5-Hexenyltrimethylsilane $CH_2=CHCH_2CH_2CH_2CH_2Si(CH_3)_3$ (XVIII). To the Grignard reagent prepared from 2.5 g of Mg and 19.6 g of (3-bromopropyl) trimethylsilane [8], 26 g of C_3H_5Br was added. The ether was distilled off, and the residue was heated at about 100° for 17 hours. The product was 6.5 g (41.5%) of (XVIII), b.p. 157-160°.

	Found %:	C 68.13; 68.36;	H 12.91; 12.95;	Si 18.30; 17.67
$C_9H_{22}Si$.	Calculated %:	C 69.15;	H 12.90;	Si 17.95

SUMMARY

1. The direction of the addition of HBr to 4-alkenylsilanes has been established, and at the same time a new method has been found for the preparation of 3-alkenylsilanes by the dehydrobromination of trialkyl(4-bromoalkyl)silanes with alkali.

2. By this method, and also by the reaction of Grignard reagents prepared from trialkyl(1-chloroalkyl) silanes with allyl bromide and with 2-methylallyl chloride, six new 3-alkenylsilanes have been prepared.

3. The first 5-alkenylsilane has been prepared.

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N. D. Zelinsky Institute of Organic Chemistry of the U.S.S.R. Academy of Sciences

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SYNTHESIS OF SODIUM TETRAPHENYLBORON

A. N. Nesmeyanov and V. A. Sazonova

It is well known that sodium tetraphenylboron [1] is of interest in analytical chemistry as a reagent for the potassium ion. In this short paper we describe a more convenient method for the preparation of sodium tetraphenylboron. In a previous paper [2] we have described the reaction of phenylmagnesium bromide with potassium fluoborate, which leads to the formation of potassium tetraphenylboron. Sodium fluoborate reacts similarly with the organomagnesium compound:

$$NaBF_4 + 4C_6H_5MgBr \longrightarrow NaB(C_6H_5)_4 + 4MgBrF.$$

This reaction gives a 62-68% yield of sodium tetraphenylboron.

EXPERIMENTAL

Sodium fluoborate (6 g) was added to an ether solution of phenylmagnesium bromide, prepared from 7 g of magnesium, 46 g of bromobenzene, and 150 ml of absolute ether. The reaction mixture was stirred for 1.5-2 hours, and was then poured into water, or, preferably, saturated NaCl solution. The ether layer was separated, and the aqueous part was extracted twice with ether. The ether extracts were united, and the ether was removed under reduced pressure. The residue crystallized; it was dried, and washed free from biphenyl by means of chloroform. The product was 12.5 g of a crystalline substance containing 96% of $NaB(C_6H_5)_4$.

For purification the substance was dissolved at 0° in ether (freed from alcohol and dried over $CaCl_2$) to which 1-2 drops of water had been added [$NaB(C_6H_5)_4$ is poorly soluble in absolute ether].

The ether solution was filtered, and heated to the boil. A crystalline precipitate of sodium tetraphenylboron then formed. It was filtered off and vacuum-dried.

Found %: Na 6.70; 6.53
$C_{24}H_{20}BNa$. Calculated %: Na 6.72

A filtered aqueous solutionof 0.6 g of the preparation was added to an aqueous solution of 0.0745 g of KCl at 50°. The precipitated $KB(C_6H_5)_4$ was filtered off (through a No. 3 or No. 4 crucible), washed with water, and dried. The amount of $KB(C_6H_5)_4$ obtained was 0.3576 g, and the calculated amount was 0.3578 g.

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M. V. Lomonosov Moscow State University

* See Consultants Bureau Translation, page 301.
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CURRENT EVENTS

AT THE DIVISION OF CHEMICAL SCIENCE OF THE ACADEMY OF SCIENCES OF THE USSR

A general meeting of the Division of Chemical Science of the Academy of Sciences of the USSR took place on October 21 and 22, 1954, under the chairmanship of the Academician-Secretary of the Division, Academician M. M. Dubinin. It was devoted to the reading of papers by Academician A. E. Arbuzov — on the problem of the synthesis of insecticides — by Academician S. I. Volfkovich — on a new technical process for the manufacture of fertilizers — and by the chief editor of the abstract journal "Chemistry", V. V. Serpinsky, who presented a report in connection with the first anniversary of the issue of the journal.

Academician A. E. Arbuzov discussed the investigations carried out by him and his students at the Kazan Affiliated Institute of the Academy of Sciences of the USSR on the synthesis of new organophosphorus compounds having practical importance as insecticides.

Matters relating to the structure of organic derivatives of phosphorous acid have occupied A. E. Arbuzov since 1903. One of A. E. Arbuzov's most important discoveries is the isomerization of full esters of this acid into esters of alkylphosphonic acids. This reaction, which has been given the name of "the Arbuzov rearrangement", has been studied by many chemists, here and abroad, and more than 300 examples of this rearrangement have now been investigated. As a result of investigations by A. E. and B. A. Arbuzov from 1928 onwards on compounds derived from or related to phosphorous acid, a new and extremely simple method has been found for the preparation of free radicals of the triarylmethyl series. In the course of the investigation of the mechanism of the new reaction, esters of hypophosphoric and pyrophosphorous acids were prepared for the first time. By the addition of one or two atoms of sulfur to these compounds, new classes of organophosphorus compounds were obtained, and these were shown later to be very powerful insecticides. Of the many hundreds of these compounds that have been synthesized in recent years, particular interest is presented by tetraethyl pyrophosphate (TEPP), tetraethyl dithiopyrophosphate ("Dithio"), tetraethyl monothiopyrophosphate ("Pyrophos"), and octamethyl tetraamidopyrophosphate ("Octamethyl"). In the course of the study of these compounds, the methods for their synthesis have been simplified. Great interest has been shown recently in "Octamethyl", an insecticide having a so-called systemic action.

Academician S. I. Volfkovich discussed a new method of preparing phosphorus fertilizers and feeding stuffs for livestock by the treatment of natural phosphates (apatite and phosphorites) with steam at high temperature in presence of small amounts of mineral additives. In this hydrothermal process apatite is broken down with evolution of gaseous fluorine, and a form of phosphate that is readily assimilated by plants is formed.

Until now, the most widely used methods of manufacture have been based on the treatment of natural phosphates with acids; some electrothermal and "alkalithermal" methods have been used on a small scale. The method studied by the speaker in conjunction with workers from the Fertilizer and Insectofungicide Institute and the Chemical Technology Department of the Moscow State University does not require acids, alkalis, or electrical energy in appreciable amount, but requires only the usual fuels (fuel oil, natural gas, or coal).

Laboratory and pilot experiments have shown that a dry, free-running product containing 32-36% of citric-soluble phosphoric oxide and not more than 0.1% of fluorine (larger amounts are harmful to many animals) can be obtained by this method. The new fertilizer is about twice as rich in phosphorus as superphosphate and Thomas slag, and it is of great interest in relation to the soils of the northern belt of the Soviet Union.

The work was carried out by S. I. Volfkovich together with N. N. Postnikov, V. V. Illarionov, R. E. Remen, A. A. Ionass, N. D. Talanov, and others.

In his paper, the chief editor of the abstract journal "Chemistry" V. V. Serpinsky emphasized the important part played in the organization and publication of the journal by its first editor, B. N. Rutovsky, who had recently died. He discussed the present state of the publication of the journal and the prospects for its further improvement in the future.

The speaker emphasized the exceptional significance for chemists of the publication of an abstract journal in view of the enormous scale on which the publication of periodical literature on chemistry and related sciences was proceeding throughout the world. The total number of journals from which the material for the new abstract journal

was gathered was approximately 5,500. The speaker stated that chemical abstracting has a long history, and he referred to "Chemisches Zentralblatt", which had its 125th anniversary in 1954, "Chemical Abstracts" which has been published since 1907, and a number of other abstract journals in English, French, Czech, Japanese, Spanish (published in Mexico), Rumanian, Hungarian, and other languages. Also, as is well known, numerous abstract journals are published for separate branches of chemical technology (rubber, plastics, leather, sugar, acids, and so on).

The organization of an Institute of Scientific Information within the system of the Academy of Sciences of the USSR with the function, among others, of publishing journals has provided investigators with an abstract journal in Russian, which has made it much easier for Soviet scientists, technologists, and teachers to follow the development of many branches of world science: for the Soviet abstract journal is published in numerous series — chemistry, physics, mathematics, astronomy, geodesy, mechanics, geography, geology, biology — and a new series on biochemistry is being prepared. This, the speaker pointed out, is the fundamental difference between the Soviet journal and other abstract journals. This enormous venture has been associated with the overcoming of considerable difficulties. Every day in the editorial department, the registration, examination, and marking of thousands of different journals are proceeding, and at the same time hundreds of abstracts are being written, edited, printed, and corrected. There are still further incidental difficulties, especially with respect to the translation of certain scientific and technical terms into Russian.

An important object, which has not yet been reached, is the attainment by the journal of what the speaker called "a stationary state", in which the journal will be able to print as much material as it obtains. When this has been achieved (partly by increase in volume), there will be a planned reduction in the time between the appearance of the original paper and the appearance of the abstract of that paper. It is then proposed to narrow the scope of the material to be printed in the journal "Chemistry". For example, matters concerning the atomic nucleus, the physical properties of solids, and some other subjects, will be found only in the journal "Physics". Certain mineralogical matters will be found in the journal "Geology and Geography". The possibility cannot be excluded of the occurrence of duplication of material, and, within limits, this is inevitable, for the chemist rightly expects that a single abstract journal will cover all of the subjects that interest him. One problem, the satisfactory solution of which would greatly facilitate the use of the journal, is correct rubrication. The editorial board hopes to improve it somewhat, but cannot envisage any fundamental changes. For example, the section on natural substances will be headed "Natural Substances and Steroids".

The question arises of the need for critical appraisal in an abstract. Should there be any departure from the principle of the exclusion of critical appraisal of any sort relating to the paper being abstracted? The speaker pointed out that 100% objective abstracting was impossible, but the number of editorial comments had been insignificant (only 24 for 51,000 abstracts).

In the discussion on V. V. Serpinsky's paper, the importance of the founding of the Institute of Scientific Information within the system of the Academy of Sciences of the USSR was emphasized. The significance of the new abstract journals was also stressed, and its defects were discussed.

Corr. Member B. V. Nekrasov suggested that the lengths of the abstracts should be reduced and smaller type should be used so that a fuller coverage of material could be attained.

Prof. G. B. Boky considered that one of the defects was the nonuniformity of terms and symbols in the abstract journals of different series — "Physics" and "Chemistry", for example. Prof. G. B. Boky recommended that the Institute of Scientific Information should take an active part in the development of chemical nomenclature.

Corr. Member A. F. Kapustinsky stressed the need for an objective presentation of the contents of the papers, without any critical remarks or reservations. He considered that the section on geochemistry in the journal "Chemistry" should be extended.

Academician A. N. Frumkin considered that one of the most important problems for the journal was the attainment of a stationary state with respect to world literature; also, the publishing of fuller patent information is desirable.

Corr. Member A. P. Terenin drew attention to the need for the careful compilation of subject and formula indexes and for the systematization of chemical nomenclature.

Corr. Member Ya. I. Gerasimov suggested that the journal "Chemistry" should be issued in the form of separate sections in order to make it less costly to the reader and less bulky when kept in annual sets.

G. V. Bykov, Cand. Chem. Sci., considered that books should be reviewed and not simply listed bibliographically. He suggested also that abstracts should be given of papers on the history of chemistry.

V. I. Kuznetsov, Doc. Chem. Sci., and others recommended that abstracts should be made of theses, which are

generally difficult of access to the reader.

Among those who discussed the need for paying great attention to the abstracting of patents were Corr. Member M. I. Kabachnik, Corr. Member A. V. Novoselova, A. I. Korolev, Doc.Chem.Sci., and N. N. Vorozhtsov.

At the same time the poor coverage of technological chemistry in the journal was pointed out.

The chairman, Academician M. M. Dubinin, in summing up the discussion, particularly stressed the importance of the widest possible participation of chemists in the work of the journal. Without this, improvements cannot be effected, and this is especially true of the abstracting of scientific papers and patents in the important section of chemical technology. The Editorial Board should seek the cooperation of the active members of the Mendeleev All-Union Chemical Society and the Ministry of Chemical Industry, and they should convene a special conference on this subject. Academician M. M. Dubinin made a number of concrete suggestions relating to the increasing of the responsibility of the institutes of the Division of Chemical Science of the Academy of Sciences of the USSR for the high quality of the material in the journal.

The chief editor of the journal V. V. Serpinsky agreeed with most of the remarks that had been made, and he stated that one of the most serious defects of the journal was the inadequate development of the technological section. Measures would be taken in the near future for the removal of this defect. The Editorial Board would like to see reviews of the abstract journal "Chemistry" in the periodical press.

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Fig. 3. Crystals of barium disilicate (3% Al_2O_3, 1250°, crossed nicols).

Fig. 4. Crystals of solid solution. (3% Al_2O_3, 1240°, crossed nicols).

Fig. 5. Crystals of solid solution. (3% Al_2O_3, 1270°).

Fig. 6. Crystals of solid solution (3% Al_2O_3, 1270°, crossed nicols).

Fig. 7. Crystals of solid solution (6% Al_2O_3, 1230°.

Fig. 8. Crystals of solid solution, (6% Al_2O_3, 1240°, crossed nicols).

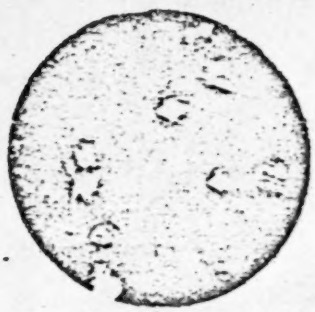

Fig. 9. Crystals of solid solution and celsian (9% Al_2O_3, 1200°, crossed nicols).

Fig. 10. Crystals of solid solution and barium metasilicate (1250°).

Fig. 11. Crystals of celsian (1380°)

Fig. 11. Crystals of solid solution and celsian (taken by reflected light)

Babinet's Principle, and the Low-Angle Scattering of X-rays by Porous Glasses. p. 19

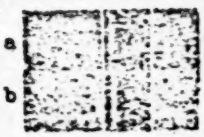

Fig. 1. X-Ray pictures: a) original specimen of highly dispersed porous glass; b) the same glass treated with KOH for (2 + 2) hours. The light band is the trace of the trap for the primary beam. The minimum scattering angle is 6,5', and themaximum is about 1,5°.

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